

ORNL Manufacturing Demonstration Facility
Technical Collaboration **Final Report**

Synthesis of Earth Abundant Nanomaterials for Flexible Solar Cell Applications¹

Sharp Laboratories of America, Oregon State University

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Company Size: Large business

Summary

The collaboration between Sharp Laboratories of America (SLA), Oregon State University (OSU) and ORNL focused on low thermal budget pulse thermal processing (PTP) technique to develop high performance copper zinc tin sulfide (CZTS) thin film system for advanced photovoltaic (PV) applications, with the goal to develop novel fabrication processes for the manufacture of low-cost, high-performance PV modules. Significant improvements in crystallinity and morphology of nanoparticle CZTS thin films and kesterite phase control were achieved by low thermal budget photonic curing. The combination of pulse thermal processing technology and inexpensive, high performance nanoparticle coatings shows promise for the development of a sustainable CZTS PV technology.

Background

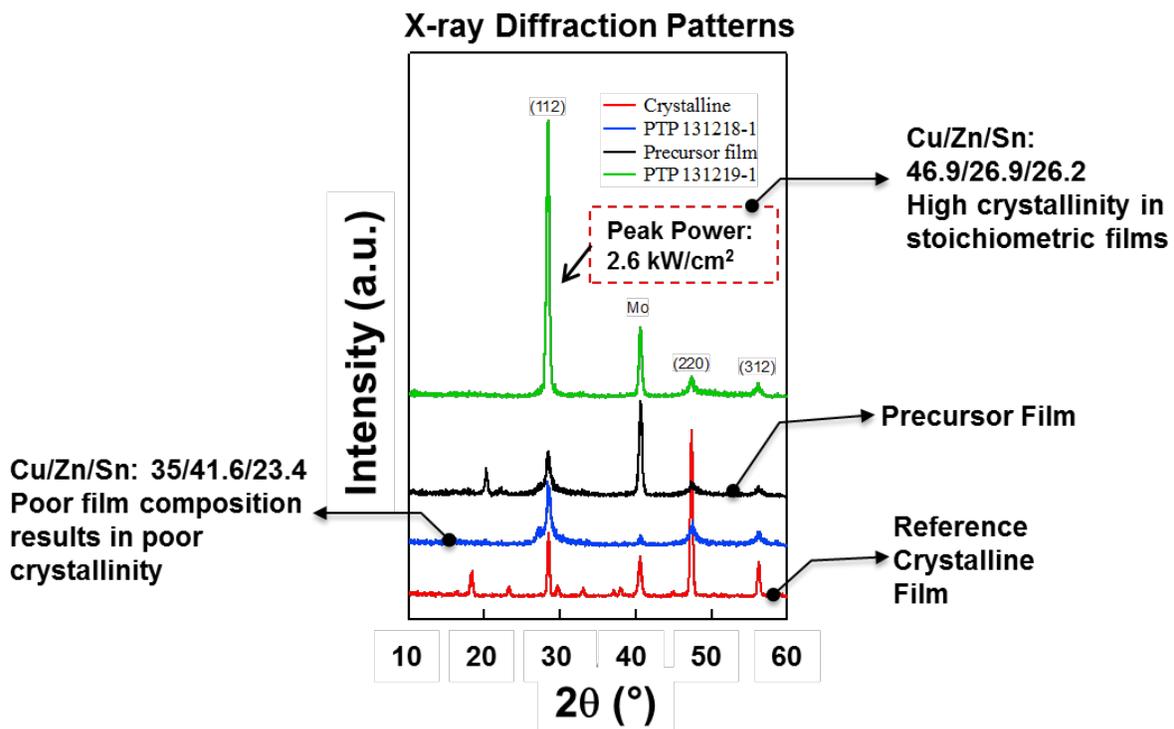
Considerable effort is being employed to reduce the levelized cost of energy for photovoltaic systems to more favorably compete with standard utility based energy sources. Manufacturing concepts are being applied to enhance performance and/or reduce cost through nanomaterials and nanostructures. Here, we investigated the impact of low temperature photonic curing on the performance of copper zinc tin sulfide/selenide (CZTS) system—a promising earth-abundant absorber layer for printed solar cells. CZTS nanoparticle inks are of interest for high performance PV cell development at low temperatures below 500°C. OSU and Sharp Labs are working together on the development of a microwave-based nanoparticle synthesis method to improve kinetics, selectivity, purity, and yield of nanoparticle for high efficiency flexible PV development. The nanoparticle ink based flexible PV technology has the potential to displace the existing technologies at efficiency level beyond 10%.

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A variety of polymeric materials are of interest for flexible photovoltaics. However, polymer substrate integration demands a significant reduction in process temperature while maintaining thin film quality. The photonic curing technique was explored to define path towards low temperature integration of solar cell absorber layer. The photonic curing system used with this project, a NovaCentrix PulseForge 3300, employs novel flash lamp and power supply technologies to generate high intensity, short duration broadband light to achieve high processing temperatures required for thin film densification, recrystallization and annealing, but without damaging the underlying low-temperature substrate material or co-integrated electronics. The combination of nanoparticle thin film processing technology and low temperature PTP annealing technique has been explored as a key solution to overcome the major limitations of the current PV technologies while meeting the critical requirements for manufacturing technology integration.

Technical Results

Nanoparticle thin films are of great interest for printed solar applications due to band gap tunability, in-situ composition control, and low-cost processing characteristics. CZTS nanoparticles were synthesized in a continuous flow mesofluidic reactor and suspended and ultrasonicated in hexanethiol, at a particle concentration of 50mg/ml of solvent. CZTS nanoparticle films, approximately 1.3 microns thick, were deposited by spin-coating onto molybdenum-coated (800nm) glass slides. Low thermal budget curing technology was explored for the crystallization of nanoparticle thin films. The sintering process-window was established in terms of the impact of processing parameters on the crystallinity, composition, and microstructure of CZTS nanoparticle thin films. The crystallinity of CZTS nanoparticle films, deposited on Mo-coated substrate, was analyzed by x-ray diffraction technique to evaluate the phase formation kinetics for advanced solar-cell absorber development. A brief summary of the main findings follows.

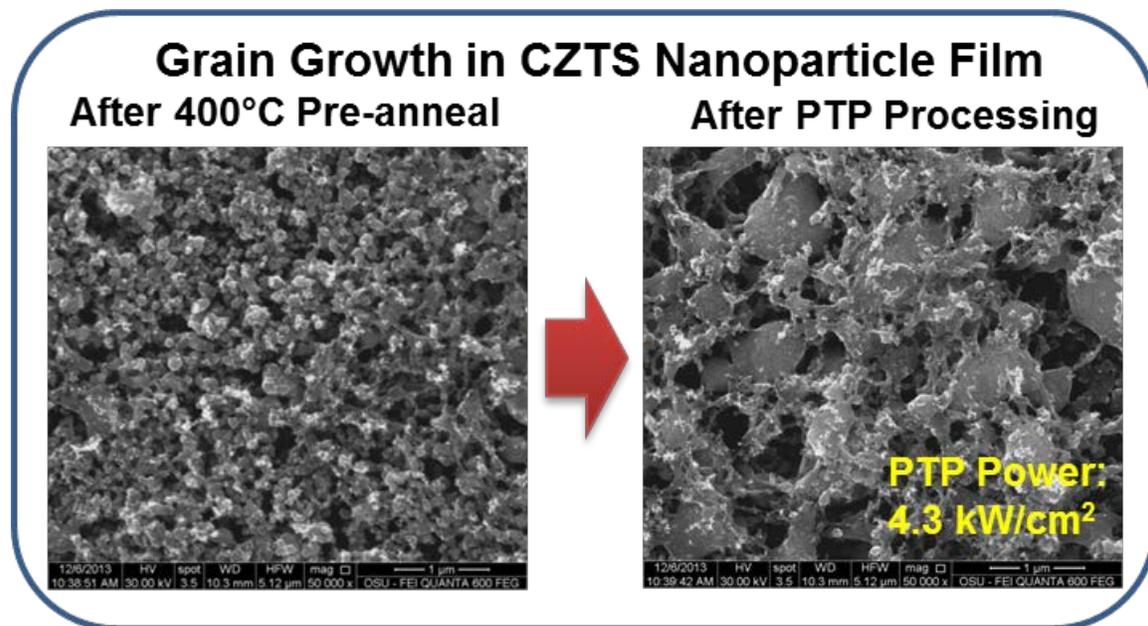


Impact of Low Thermal-Budget Photonic Curing on CZTS Thin Film Crystallinity

- Established low thermal budget PTP process-window for improved crystallization of CZTS thin films
- Observed X-ray diffraction peaks consistent with database and literature values for the CZTS crystals
- Significantly enhanced thin film crystallinity after PTP processing at a short pulse-width of 500 μ s while maintaining power-density at 2.6 kW/cm²

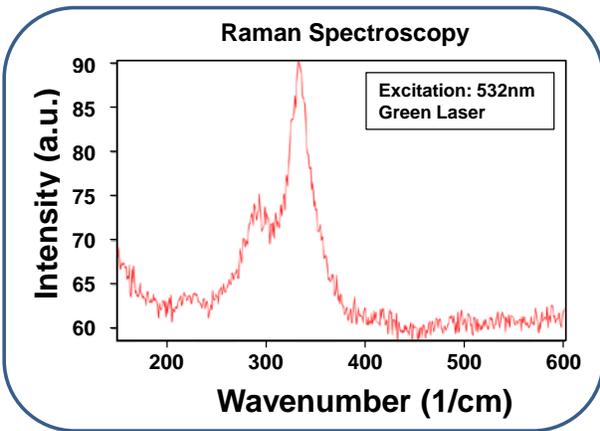
The observed crystallinity characteristics established the efficiency of photonic curing in suppressing secondary phases while promoting the kesterite CZTS phase.

Large grain growth is critical for realizing inexpensive and high efficiency CZTS-based solar cell technology. Large-grained absorber material is required to enhance solar cell efficiency by suppressing non-radiative centers. The combination of nanoparticle synthesis and photonic curing approaches was explored for high performance absorber layer development at low thermal budgets eliminating the annealing requirement in aggressive S or Se atmospheres. As highlighted in the following figure, the photonic curing was effective in significantly enhancing grain growth in nanoparticle films.



Scanning Electron Microscopy: Significant grain growth in CZTS nanoparticle films after photonic curing.

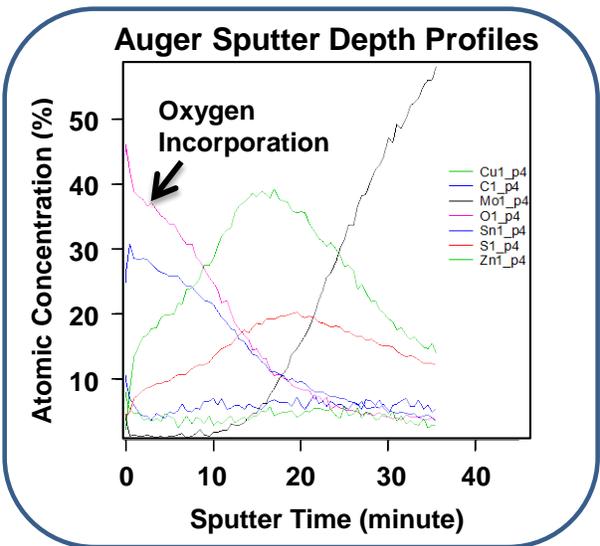
Single phase CZTS thin film development is essential to realize a high-efficiency solar cell device. Raman spectroscopy, a sensitive characterization tool to establish bonding structure in thin film structures, was performed to analyze CZTS phase-purity. Additionally, mixed compositional phases, indistinguishable in x-ray diffraction patterns, can be differentiated. The low-thermal budget photonic curing offers a unique process space to suppress secondary phases in multicomponent thin film structures while promoting large grain growth and stoichiometric phase formation.



Raman Spectroscopy:

- Raman spectroscopy was used to analyze and confirm the formation of CZTS phase
- Raman data collected using a 532 nm green laser to analyze chemical bonding
- A strong peak at 338 1/cm and the shoulder at 289 1/cm are indicative of kesterite CZTS; results consistent with x-ray diffraction analysis

Low thermal budget sintering techniques are required for nm-scale inter-layer diffusion control in multilayer solar cell devices. The composition profile of CZTS thin films was examined by Auger electron spectroscopy to establish the impact of low thermal budget photonic curing on bulk composition and elemental interdiffusion.



Auger Sputter Depth Profile:

- PTP is effective in controlling diffusion of reactive elements in thin films
- However, surface oxidation is evident even for a pulse-width of 500µs
- Future investigation should focus on controlled PTP processing in an environmental chamber to prevent oxygen incorporation

Impacts

CZTS is a potential absorber candidate for low cost thin film solar cells due to its favorable optoelectronic properties and the relatively high abundance of its constituent elements. CZTS is isoelectronic with $CuIn_xGa_{1-x}Se_2$ (CIGS), a close structural analog that is currently employed in commercial thin film solar modules, where two trivalent indium or gallium ions are replaced by a divalent zinc and tetravalent tin ion. In 2011, the prices of indium and gallium were roughly 300 times the price of zinc and 25 times the price of tin. If large quantities of these materials are used in the future for high volume solar cell production, CZTS would likely provide significant cost advantages compared to CIGS due to the relatively lower cost of zinc and tin, provided the solar cell efficiency is comparable. The photonic curing technique explored in the present investigation shows promise for low-thermal budget solar cell integration exploiting the

evolving nanomaterials technology. The combination of nanoparticle CZTS thin films and photonic curing technique holds promise for non-vacuum deposition of CZTS absorber films for low-cost thin film solar cells.

Research here addresses objectives by DOE's Advanced Manufacturing Office for developing broadly applicable manufacturing processes that reduce energy intensity and improve production. An advanced solar cell technology based on CZTS holds promise as cost and efficiency will dictate the technology suitability for terawatt level deployment of photovoltaics. Flexible solar cell technologies will offer potential benefits in both new product applications and potentially lower manufacturing costs. The PV technologies based on earth-abundant thin film solar cell materials have the potential to displace existing technologies based on CdTe, CIGS, and Si material at efficiency levels beyond 15%.

Conclusions

ORNL, OSU, and Sharp Labs collaborated on the low thermal budget processing of CZTS nanoparticle thin films for advanced PV applications exploiting pulse thermal processing technology. Significant improvements in crystallinity and morphology of nanoparticle CZTS thin films and kesterite phase control by low thermal budget photonic curing show promise for advanced solar cell applications. The present investigation is an important piece of foundational work in development of light-weight, flexible, and conformal solar cells. The combination of pulse thermal processing technology and inexpensive, high performance nanoparticle coatings shows promise for the development of a sustainable CZTS PV technology.

About the Company

Oregon State University (OSU) is the leading public research university in Oregon, with \$263 million in external funding in the 2013 fiscal year. OSU welcomes a diverse student body of over 26,000 students from across Oregon, all 50 states and more than 100 countries.

Sharp Laboratories of America (SLA) is the U.S. research and development (R&D) subsidiary for Sharp Corporation of Japan. Since 1959, Sharp has led the solar electric industry with efficient, affordable systems: from the world's first solar-powered calculator to solar-powered residential and commercial applications.

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