

Annealing of Copper Zinc Tin Sulfide Thin Films

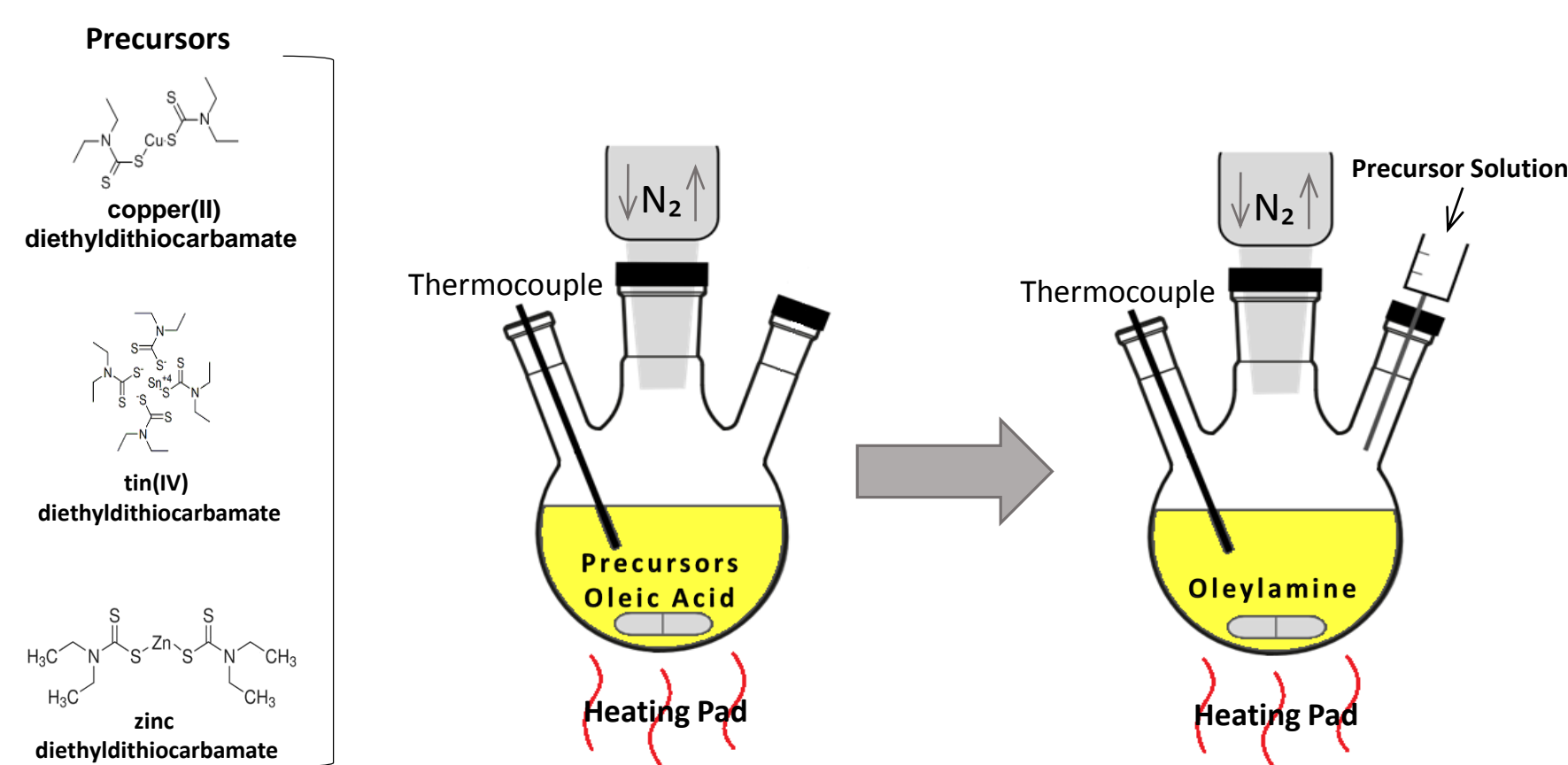
Michelle Smeaton, Bryce Williams, Eray Aydil

Department of Chemical Engineering and Materials Science, University of Minnesota

CZTS as a Solar Absorber

Copper Zinc Tin Sulfide (CZTS) is a low cost, environmentally friendly alternative to other thin film solar cell materials such as CIGS or CdTe because of its nontoxic, earth abundant components. Ideal films for solar absorption have large, consistent grains which allow for uninhibited electron transport. To this end, we have explored variations of two annealing methods which cause the nanocrystals to grow and merge to create a large grain polycrystalline film.

Nanocrystal Synthesis

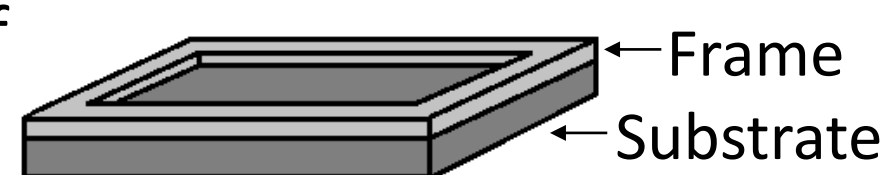


- Nanocrystals are synthesized in a schlenk line apparatus.
- A nitrogen environment prevents the formation of oxides.
- Injection of precursor solution into hot oleylamine causes simultaneous decomposition of precursors and formation of CZTS nuclei thus creating a single phase.
- Nanocrystal size is tunable by varying oleylamine temperature. Here, 45 nm nanocrystals were formed with a temperature of 340°C.

Coating Preparation

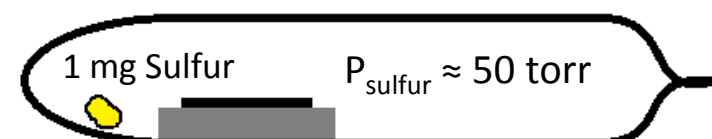
Films were created by drop casting nanocrystal dispersions onto molybdenum coated soda lime glass.

60 μ L of a nanocrystal dispersion was drop cast into the center of a metal frame clamped to the substrate.



Annealing Methods

Thermal



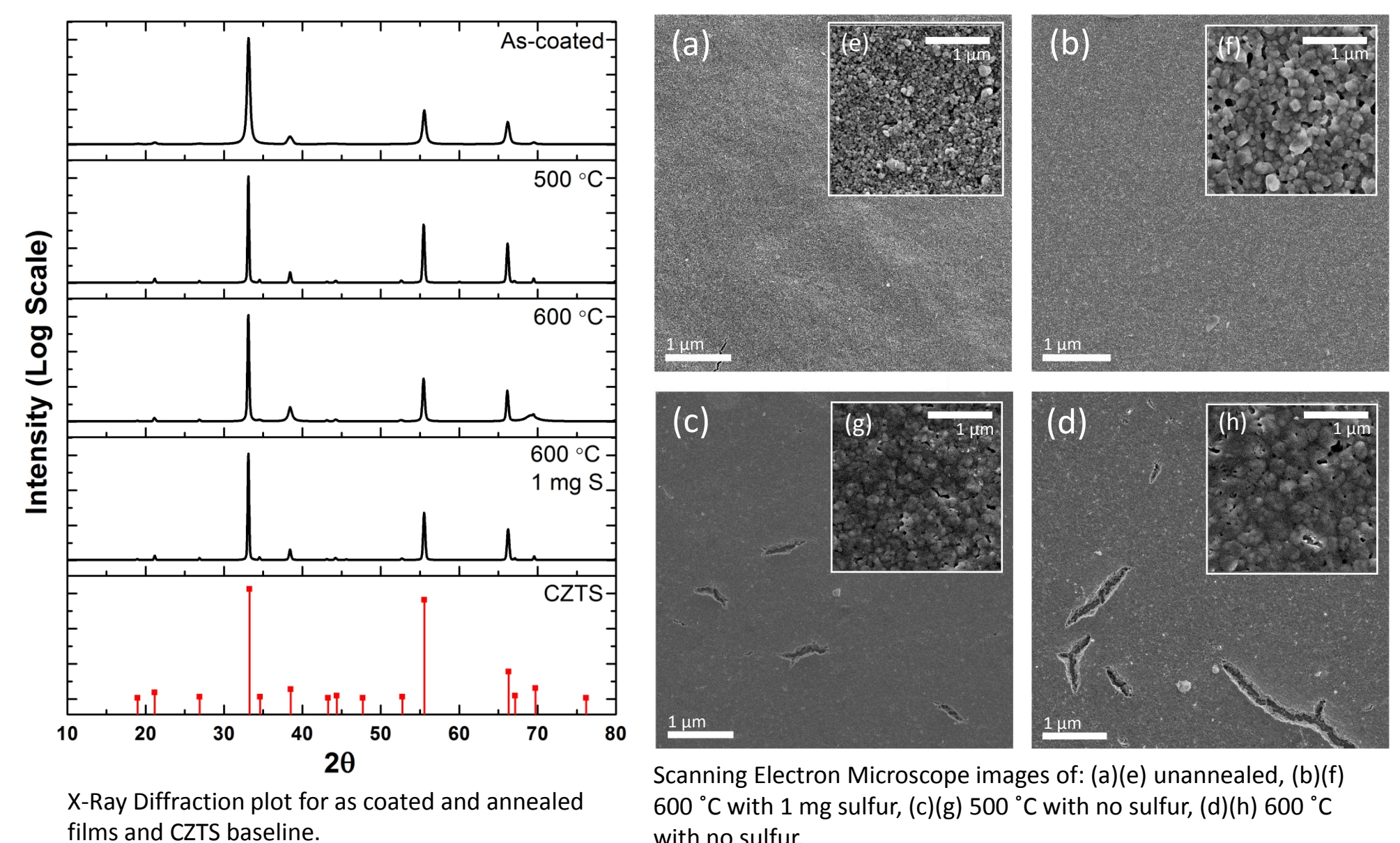
Samples were placed inside quartz tubes with or without 1mg of sulfur, evacuated and flame sealed. The ampoules were placed in a furnace and annealed at 500-600°C for one hour then allowed to cool naturally.

Intense Pulsed Light

IPL uses short (~ms), high intensity pulses of visible light produced by a Xenon flash lamp to heat up absorbing materials, in this case, CZTS.



Thermal Annealing

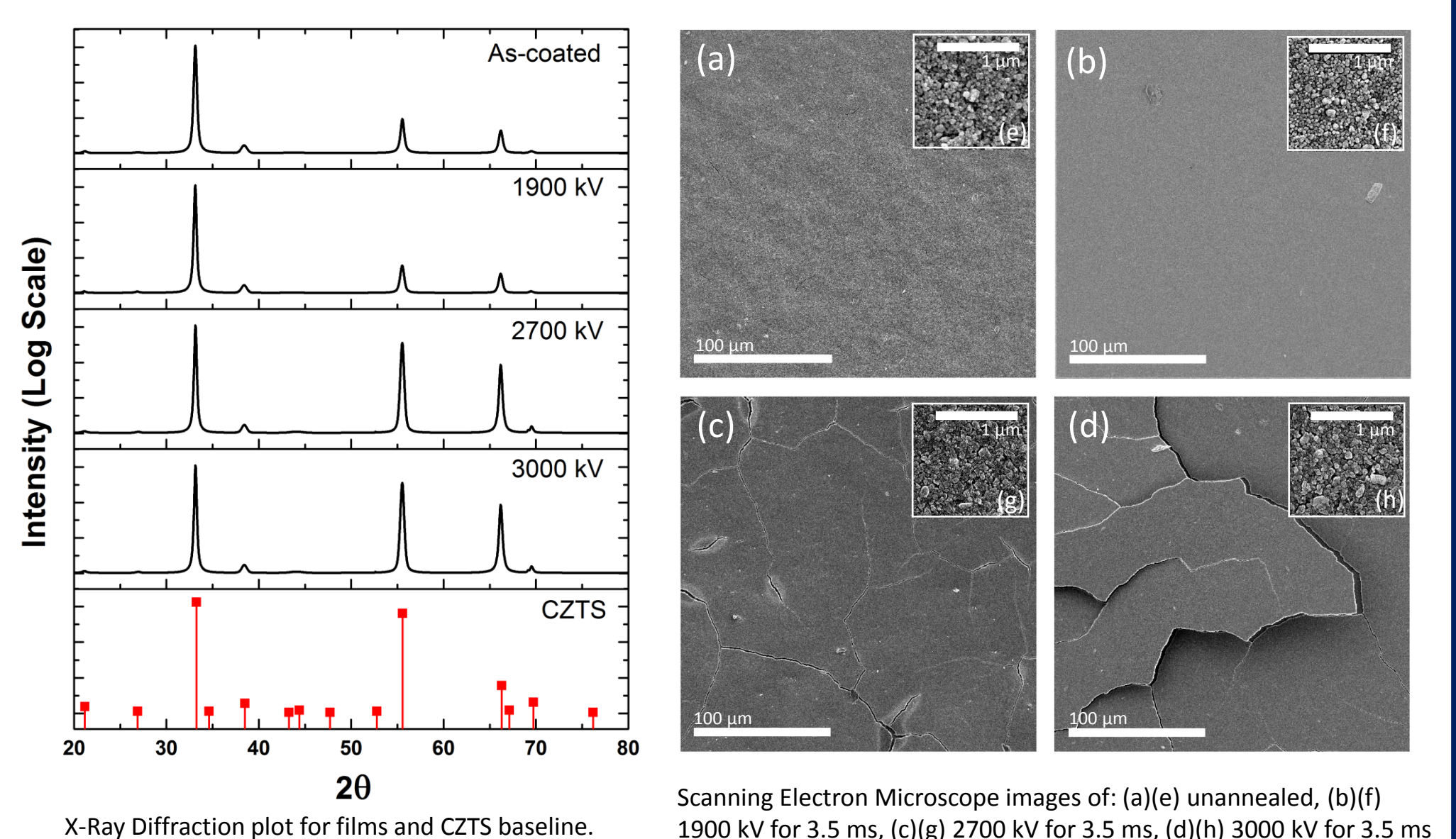


X-Ray Diffraction plot for as coated and annealed films and CZTS baseline.

Scanning Electron Microscope images of: (a)(e) unannealed, (b)(f) 600 °C with 1 mg sulfur, (c)(g) 500 °C with no sulfur, (d)(h) 600 °C with no sulfur.

X-ray diffraction confirmed that the films consisted of CZTS both before and after annealing in all cases. All three annealed films showed significant nanocrystal growth as compared to the unannealed sample. However, the samples annealed without sulfur also showed some cracking which increased with increased temperature. The sample annealed in a sulfur atmosphere did not crack.

Intense Pulsed Light Annealing



X-Ray Diffraction plot for films and CZTS baseline.

Scanning Electron Microscope images of: (a)(e) unannealed, (b)(f) 1900 kV for 3.5 ms, (c)(g) 2700 kV for 3.5 ms, (d)(h) 3000 kV for 3.5 ms

X-ray diffraction confirmed that the films consisted of CZTS crystals both before and after annealing. It also showed an increase in crystallinity for films annealed at >1900 kV indicated by the increased height of the peaks. There was no noticeable change in the size of the nanocrystals in any annealed film. There was however a clear progression in the cracking of the films. As the annealing energy was increased, cracks formed and the film began to pull away from the substrate along those cracks creating a bubbling effect.

Acknowledgements

This project was supported by the University of Minnesota Undergraduate Research Opportunity Program (UROP) and completed with the use of the UMN Characterization Facility.