Tin monosulfide (SnS) is a promising semiconductor material for low-cost conversion of solar energy, playing the role of absorber layer in photovoltaic devices. SnS is, due to its high optical damping, also an excellent semiconductor candidate for the realization of ultrathin (nanoscale thickness) plasmonic solar cells [1].

Here, we present an important step to further control and understand SnS film properties produced using low temperature ALD with Sn(acac)2 and H2S as precursors. We show that the SnS film properties vary over a rather wide range depending on substrate temperature and reaction conditions, and that this is connected to the growth of cubic (π-SnS) and orthorhombic SnS phases. The optical properties of the two polymorphs differ significantly, as demonstrated by spectroscopic ellipsometry [2].

**Results**

**Effect of H2S dose and temperature on SnS growth**

- The crystal structure and morphology undergoes a notable evolution as the H2S dose varies. Cubic SnS forms at high H2S dose.
- The grain size of the SnS increases with increasing growth temperature.
- At the highest temperature, the surface is dominated by blade-like grains with a resulting high roughness.

**Crystal structure of cubic SnS versus thickness**

- Films with mainly cubic phase SnS is formed at 120 °C using a long (5 s) H2S pulse length.
- Grains are columnar and extend over the entire film thickness (42-43 nm for 1000 cycles) with more or less vertical grain boundaries.

**Spatial distribution of the SnS phases**

- As the sampling depth increases along with the angle of incidence up to 0.5°, the relative intensities of the cubic SnS (222) and (400) peaks rise for a sample with intermediate (1.6 s) H2S dose.
- This suggests a gradient with a more cubic phase near the bottom of the film and a more orthorhombic phase towards the SnS surface.
- The bottom of the layer is compact and void free. The top layer on the other hand exhibits high roughness with protruding blade-like grains.

**Optical properties**

- Direct forbidden optical bandgap of 1.64 eV for the cubic SnS phase based on linear extrapolation in a Tauc plot.
- An exponential, Urbach type dependence for orthorhombic SnS over at least two decades, with a tail width of 0.3 to 0.4 eV.
- The origin of the tail is ascribed to the nanoscale structural disorder of the blade-like morphology, to sulfur vacancies of the orthorhombic SnS, or to their combination.

**Conclusions**

- An ALD process for orthorhombic and cubic phases of SnS thin film deposition, using sequential exposures of Sn(acac)2 and H2S precursors.
- For the first time SnS of cubic phase is obtained by ALD at saturated conditions. A direct forbidden band gap of 1.64 eV is observed.
- Uniform SnS thin films over large area are achieved with controlled thickness and crystallographic phase on Si and glass substrates.

**References**


**Acknowledgement**

Financial support from The Swedish Research Council (621-2014-5599) is gratefully acknowledged.