

Supplemental Information: Semiconducting properties of spinel tin nitride and other IV_3N_4 polymorphs

Synthetic Details:

Sn_3N_4 films were grown by radio-frequency (RF) reactive sputtering of a 2-inch tin metal target in a nitrogen and argon atmosphere. The power supplied to the target was 25 W. The flow rate of nitrogen was 10 sccm, and the flow rate of argon was also 10 sccm. The chamber pressure was 20 mTorr during depositions, and the base pressure of the chamber was 2.1×10^{-6} Torr or less. The nitrogen was sourced through an RF atom source operated at 250 W. One film grown on silicon was analyzed by Rutherford back scattering (RBS) to determine elemental composition. The anion signal is shown in Figure S1. Integration of the nitrogen signal and tin signal (not shown) produce, within the error of the technique, a stoichiometry of Sn_3N_4 .

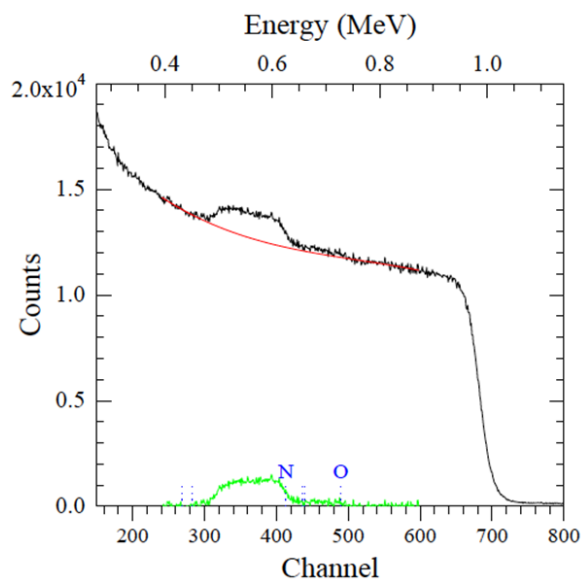


Fig. S1: Low atomic number signal from tin nitride thin film. The step in the black trace is the silicon substrate, and the background-subtracted spectrum is shown in green.

Photoelectrochemical Details:

Photoelectrochemical measurements utilized a flat-faced glass cell with a 3-electrode configuration. The FTO/ Sn_3N_4 working electrode was held at 0.2 V vs. a Ag/AgCl (saturated KCl) reference electrode in a solution containing 0.1 M Na_2SO_3 (anhydrous, 98.2%, J.T. Baker) and 0.1 M H_3BO_3 ($\geq 99.5\%$, Sigma Aldrich), adjusted to pH 9.2 using KOH. A Pt foil counter electrode (3 cm^2) was positioned approximately 1 cm away. Potential was applied and current was measured by an EG&G Princeton Applied Research VersaStat II potentiostat.

During photocurrent, the entire sample area was illuminated with a 300 W Xe arc lamp (Newport), adjusted with a calibrated Si photodiode to have an incident photon density identical

to 1 sun at energies above the Si band gap. Front illumination refers to an orientation where photons are directly incident on the Sn_3N_4 . With back illumination, photons first pass through the glass and FTO layers before entering the Sn_3N_4 . The electrode in Figure 4a was $\sim 1 \text{ cm}^2$, while the electrodes in Figure 4b were $\sim 2 \text{ cm}^2$.