

[Supporting Information]

Atomic Layer Deposition of Tin Oxide with Nitric Oxide as an Oxidant Gas

Jaeyeong Heo,^a Sang Bok Kim^a and Roy G. Gordon^{a,*}

*Department of Chemistry and Chemical Biology, Harvard University,
Cambridge, Massachusetts 02138 USA*

E-mail: gordon@chemistry.harvard.edu

Growth temperature. The thermal stability of the Sn(II) precursor has not been investigated in detail since the early study in combination with 50 wt.% H₂O₂ was focused on low temperature growth lower than 200 °C.¹ In order to determine the starting temperature of precursor decomposition, growth conditions without any NO pulse were repeated at three different substrate temperatures of 250, 280, and 310 °C. Fig. S1 shows XRF spectra for these samples where characteristic Sn L_{α1} (3.443 keV) and L_{β1} (3.662 keV) peaks are monitored. The background spectrum as a control was collected on a SiO₂/Si substrate. It is clearly seen from the Fig. S1 that the spectrum for

250 °C is almost overlapped with the standard spectrum; however the one for 280 °C shows small increase in intensity for both peaks, which is a sign of partial decomposition of the precursor. When the temperature is further increased up to 310 °C, the spectrum obviously shows more intense tin peaks. Based on these observations, it appears that this Sn(II) precursor is stable up to 250 °C and its decomposition starts at ~280 °C. If not mentioned otherwise, the film growth and characterization were done on films grown at temperatures of 250 °C or less.

Optical properties. Fig. S2a shows the optical transmission and reflection spectra of a ~110 nm-thick SnO₂ film deposited at 250 °C on a quartz substrate. The average transmission in the visible region from 400 to 700 nm was 87.2%, which is comparable to other reports for ALD-grown SnO₂.^{1,2} The Fig. S2b shows a plot appropriate for a direct transition of $(\alpha h\nu)^2$ versus photon energy, where α is the absorption coefficient and $h\nu$ is the incidence photon energy. Linear behavior is found at photon energies over 4.2 eV. The estimated band gap of the SnO₂ film was 4.23-4.27 eV. This band gap is wider than the value ~3.6 observed for undoped SnO₂.^{3,4} This widening is known as the Burstein-Moss shift, which is due to the high carrier concentration in the conduction band.⁵

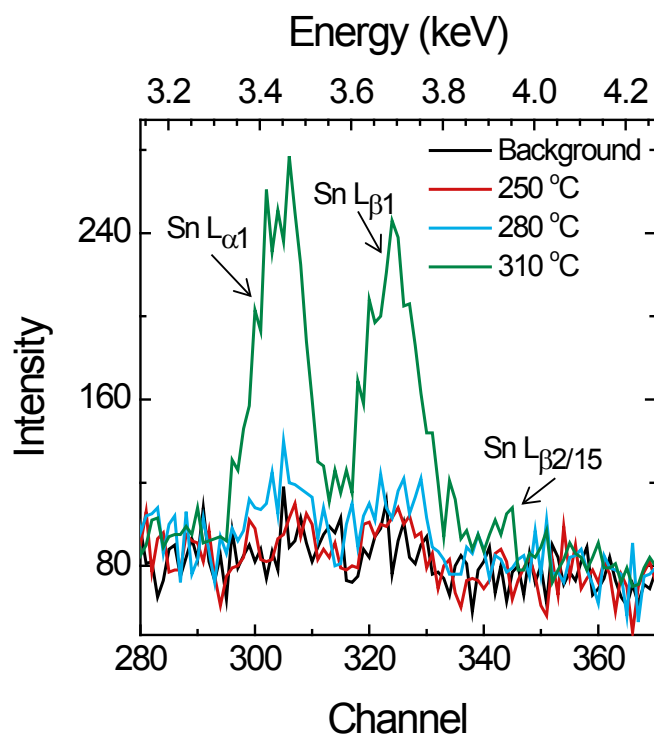


Fig. S1 XRF spectra for samples deposited at various temperatures. The background spectrum was obtained from a SiO₂/Si substrate. Three samples were exposed to Sn precursor vapor (250 cycles) without any oxidant pulse. Increases in the peak intensities of Sn L lines are noted for the 280 and 310 °C samples, which suggests thermal decomposition of the Sn(II) precursor.

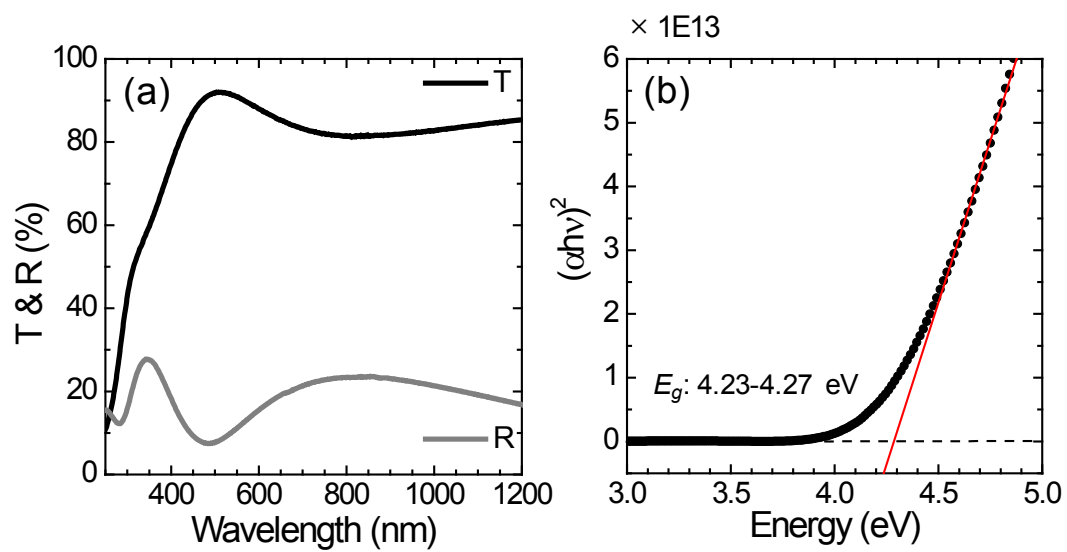


Fig. S2 (a) Transmission and reflection spectra for ~110nm-thick SnO₂ film grown at 250 °C. (b) Corresponding direct band gap plot.

References

1. J. Heo, A. S. Hock and R. G. Gordon, *Chem. Mater.*, 2010, **22**, 4964-4973.
2. J. W. Elam, D. A. Baker, A. J. Hryn, A. B. F. Martinson, M. J. Pellin and J. T. Hupp, *J. Vac. Sci. Technol. A*, 2008, **26**, 244-252.
3. R. G. Gordon, *MRS Bull.*, 2000, **25**, 52-57.
4. T. Minami, *Semicond. Sci. Technol.*, 2005, **20**, S35-S44.
5. M. Batzill and U. Diebold, *Prog. Surf. Sci.*, 2005, **79**, 47-154.