Tin Nitride Atomic Layer Deposition Using N_2H_4

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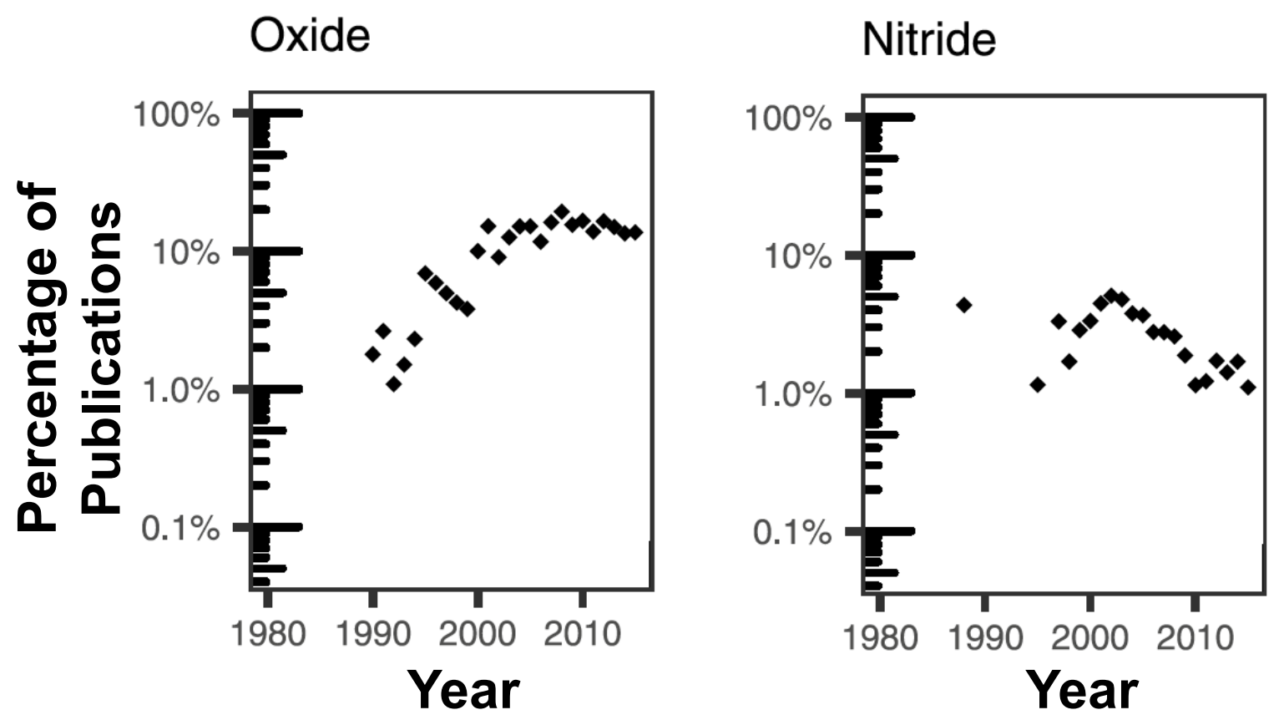
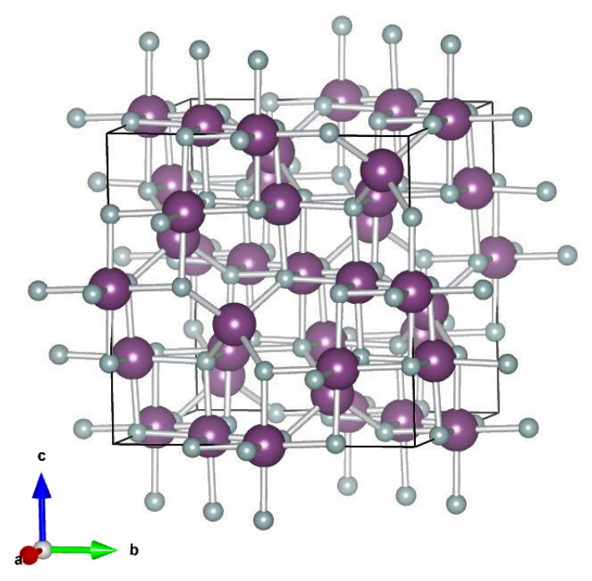
Nitrides by ALD

- GaN and related compounds opened the door to exploration of novel nitrides [1]
- Some reports of ALD nitrides by N_2 plasma and NH_3 [2], but nitrides make up only a small portion of reported processes [3]
- Sn_3N_4 is a metastable semiconductor [4] only demonstrated once by ALD [5]
- A few recent reports have demonstrated that N_2H_4 can be used as a N precursor, opening the door to new chemistries [6-8]



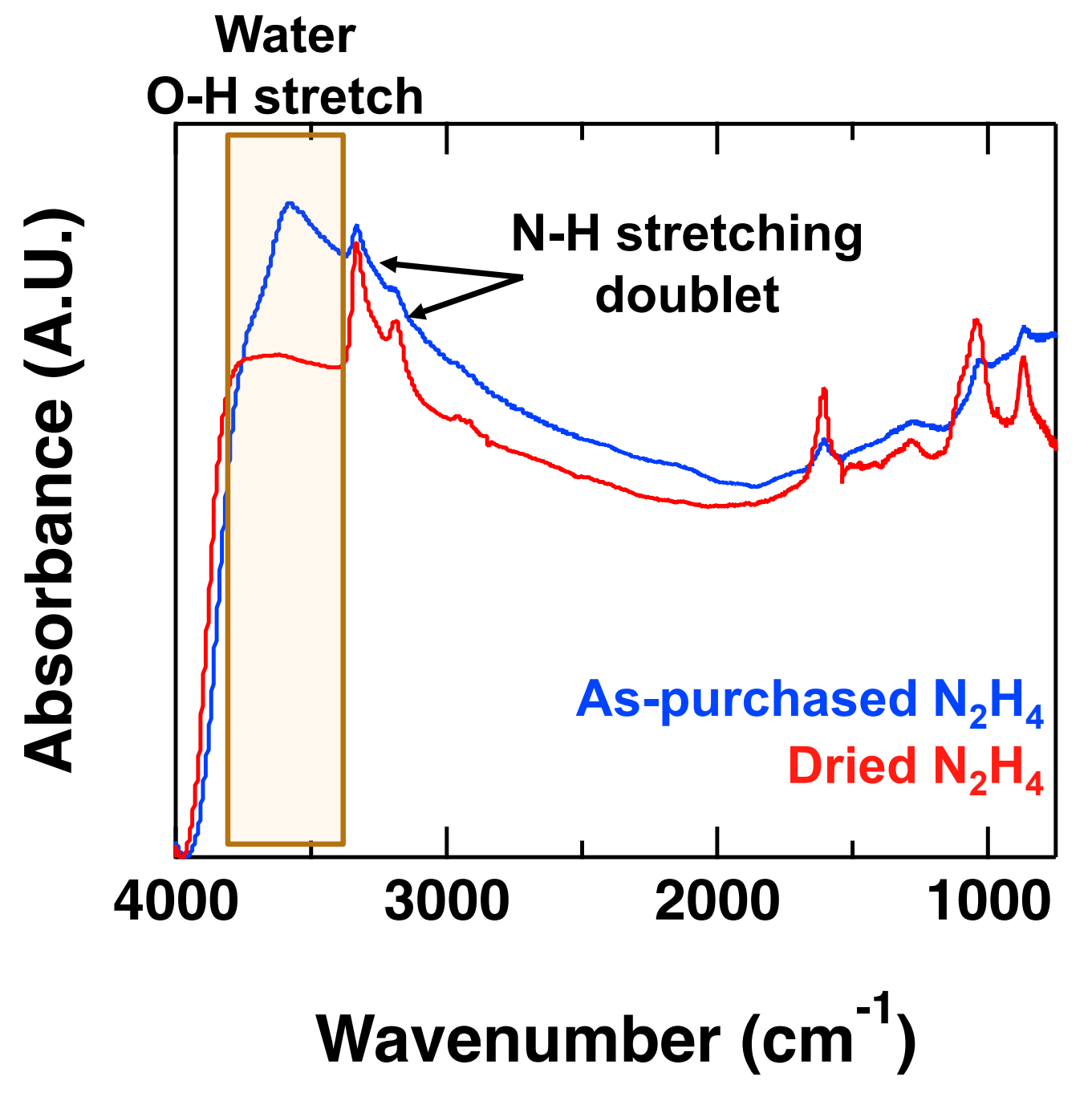
Adapted from ref. [3].



Sn_3N_4 unit cell

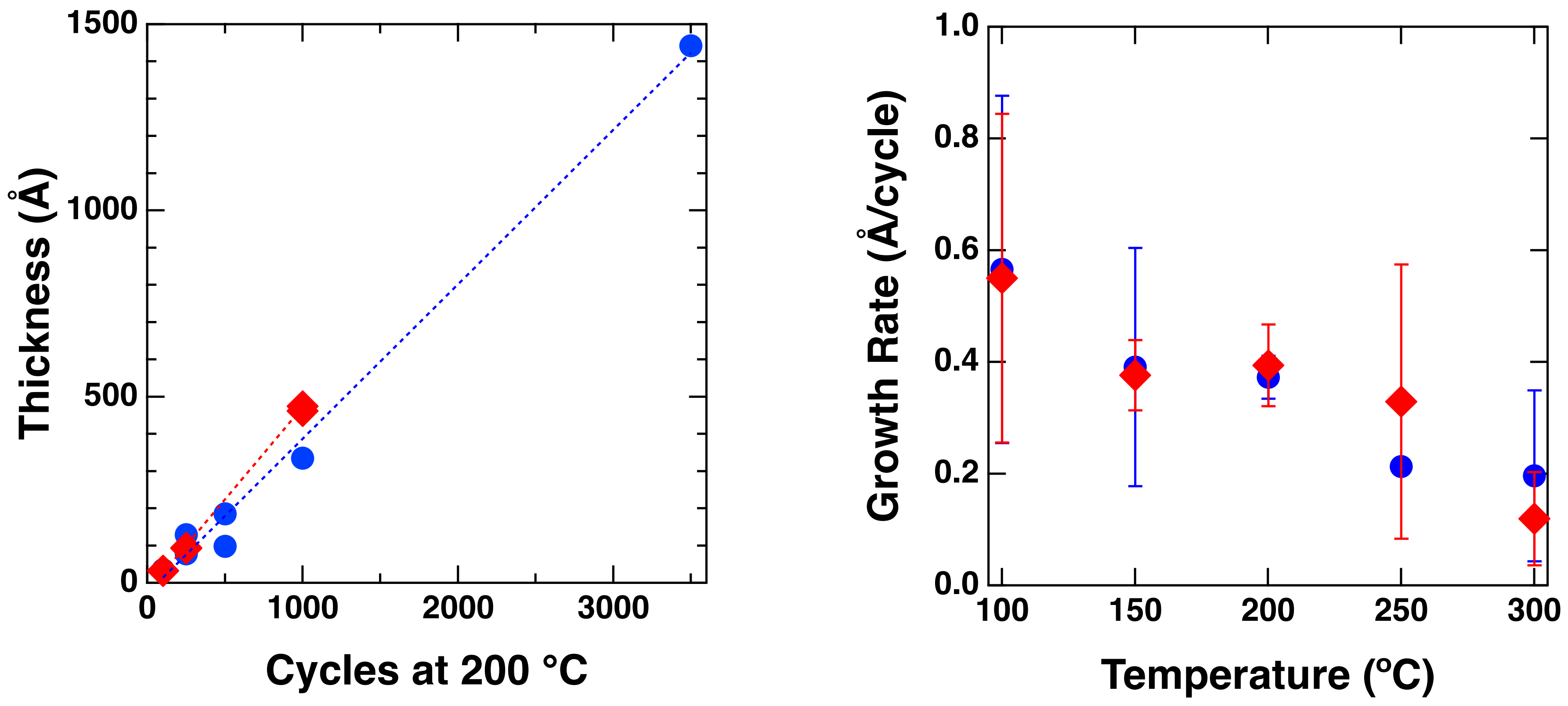
Process Development for Sn_xN_y

- Beneq TFS 200 viscous flow ALD reactor
- **Precursors:** Tetrakis(dimethylamino) tin (TDMASn) and hydrazine (N_2H_4)
  - TDMASn used for SnO_2 [9]
  - N_2 plasma and NH_3 insufficiently reactive
- N_2H_4 found to be contaminated with H_2O by IR
  - Reducing [H_2O] by reaction with CaH improves reaction consistency
  - Other procedures may be required to ensure complete removal of H_2O

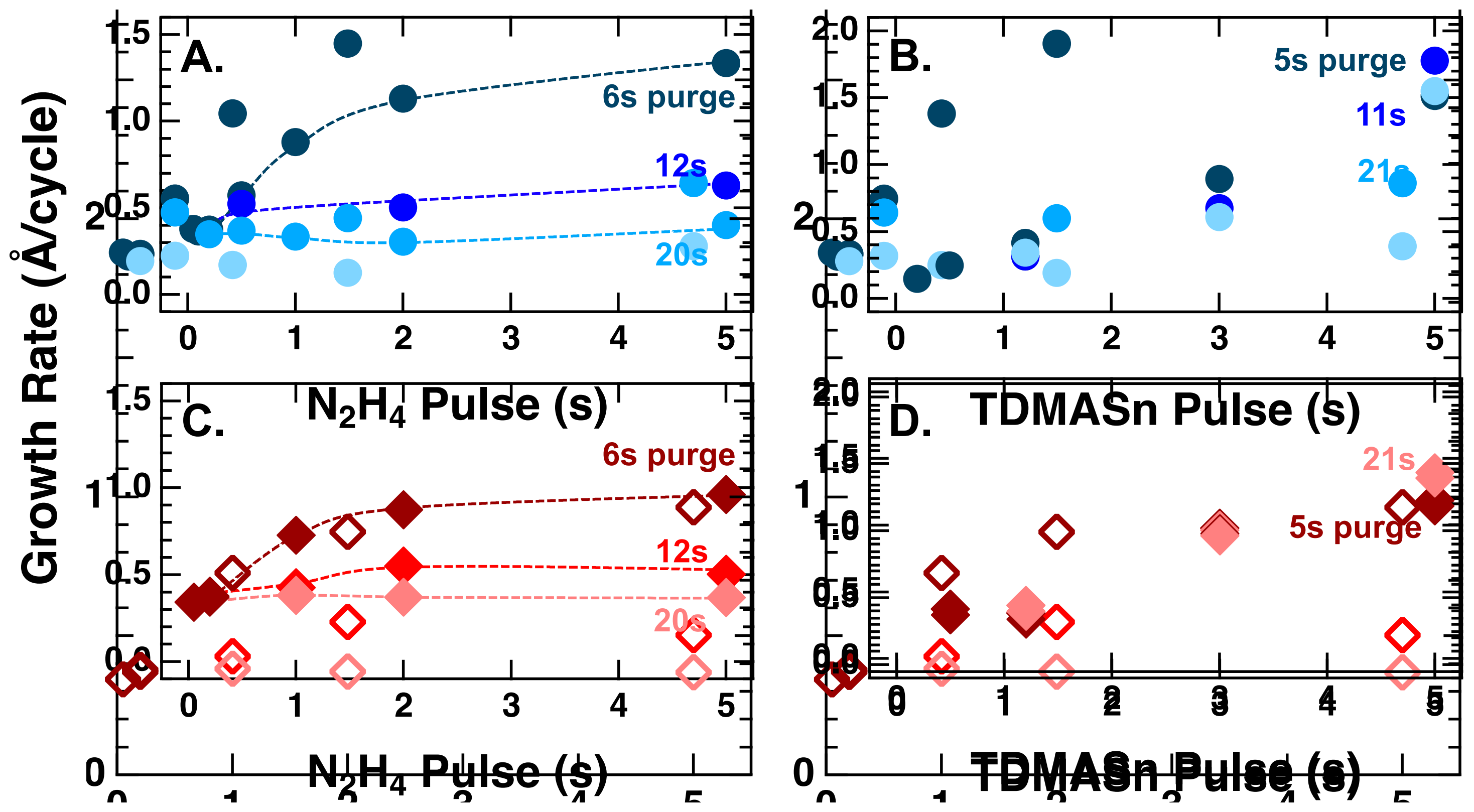


Sn_xN_y Reaction Characteristics

- Both water contaminated (**wet**) and reacted (**dry**) N_2H_4 afford linear growth per cycle (GPC) characteristics with increasing cycle number
- GPC is not flat with temperature over the studied range
  - TDMASn heated to 55 ˚C for deposition and decomposes around 300 ˚C
  - Some literature suggests presence of water impacts growth window [10]



Reaction cycle: 1 s N_2H_4 pre-pulse with 6 s purge; then repeating: 1.2 s TDMASn pulse, 5 s purge, 200 ms N_2H_4 pulse, 6 s purge. Error bars represent the standard deviation for multiple samples.



For N_2H_4, TDMASn fixed at 1.2 s pulse, 5 s purge; for TDMASn, N_2H_4 fixed at 200 ms pulse, 6 s purge. Lines in A) and C) are guides for the eye.

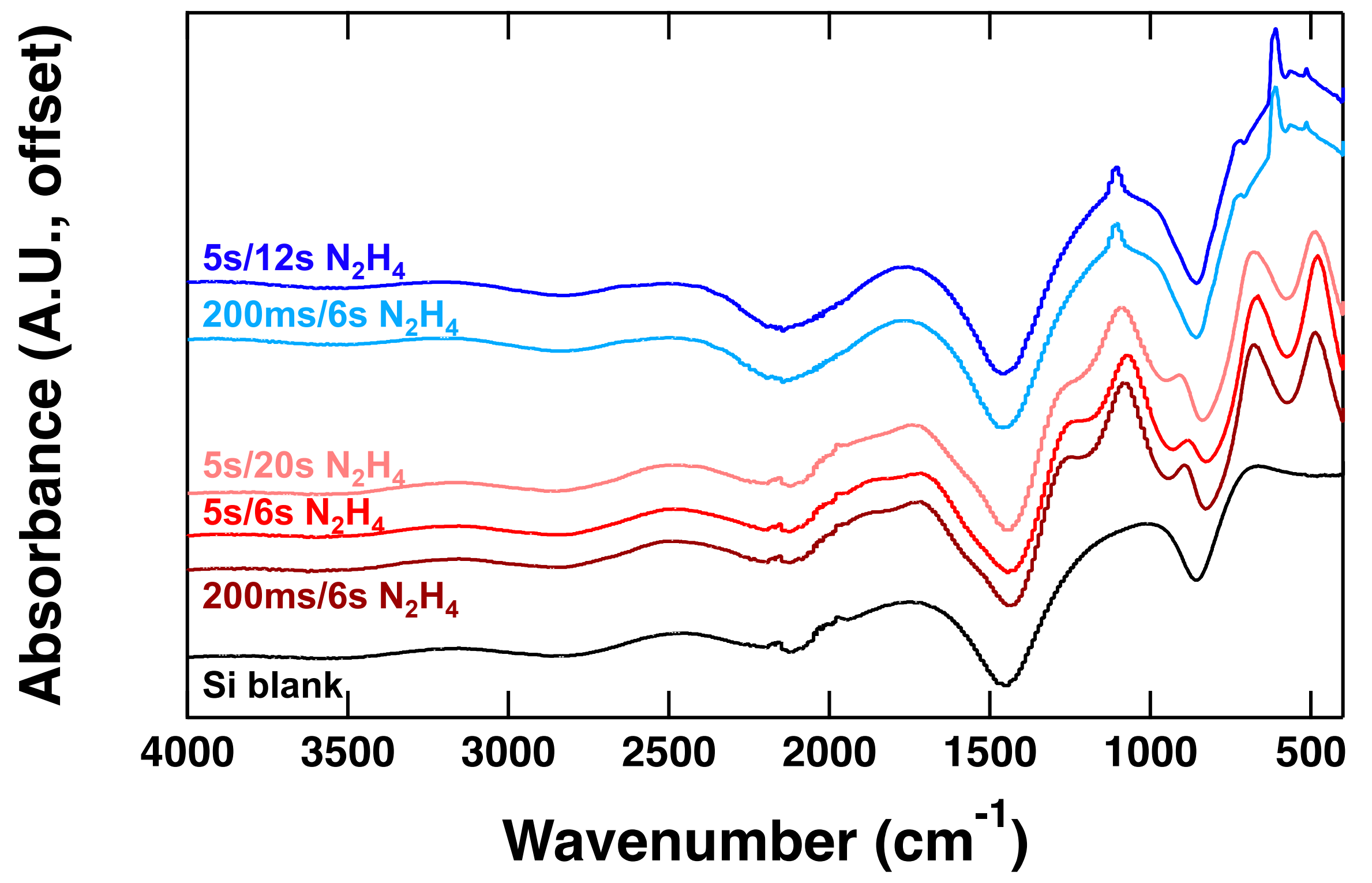
A. Long wet N_2H_4 pulses give high GPC; long purge times reduce GPC to initial saturated level
B. Long TDMASn pulses do not saturate even with long purge times with wet N_2H_4
C. Using dry N_2H_4 with short purges reduces GPC, but extending the purge length does not change
D. TDMASn GPC is reduced but does not saturate with dry N_2H_4, *but* no growth occurs without N_2H_4 pulse -- \not TDMASn condensation

Thicknesses derived from X-ray reflectivity plots and processed using Motofit in IgorPro.

Nelson, A . 'Co-refinement of multiple contrast neutron / X-ray reflectivity data using MOTOFIT.' *J. Appl. Cryst.*, **2006**, *39*, 273-276.

Sn_xN_y Characterization

- Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was used to examine films produced using both **wet** and **dry** N_2H_4
  - In both cases, the films with the longest pulse length and shortest purge are notably different than films that have the same GPC, whether that is 200ms/6s or 5s/20s pulse/purge



- X-ray photoelectron spectroscopy (XPS) was also used to examine the Sn:N ratio and look for O and C contaminants
  - All films are very low N content (target Sn:N ratio of 0.75)
  - Films grown with **wet** N_2H_4 have better Sn:N ratios but O contamination is a problem across samples

Comparison	Condition	Sn:N	Atom %			
			Sn	N	C	O
Wet vs. Dry	Standard N_2H_4: 200 ms/6s TDMASn: 1.2s/5s	**4.86**	45.95	9.46	11.28	33.09
		5.98	42.42	7.09	13.12	32.31
Wet vs. Dry	Long N_2H_4 5s/20s	**3.43**	44.48	12.96	15.52	27.04
		5.53	44.48	8.04	13.24	32.85
Large N_2H_4 vs. Large TDMASn dose	N_2H_4 5s/6s	**3.17**	42.49	13.41	23.35	17.08
	TDMASn 5s/5s	**3.64**	40.99	11.26	20.1	26.72

Conclusions

- Although drying of N_2H_4 modified growth rate, long N_2H_4 purge times are required to achieve linear GPC in long pulse limit
- Preliminary FT-IR indicates differences between films from wet and dried N_2H_4, but further verification is needed to resolve trends
- Preliminary XPS indicates very non-stoichiometric material; thicker films will be fabricated to clarify composition

[1] Zakutayev, A. Design of Nitride Semiconductors for Solar Energy Conversion. *J. Mater. Chem. A* **2016**, *4*, 6742–54.
[2] Miikkulainen, V. et al. Crystallinity of Inorganic Films Grown by Atomic Layer Deposition: Overview and General Trends. *J. Appl. Phys.* **2013,** *113*, 021301.
[3] Alvaro, E., Yanguas-Gil, A. Characterizing the Field of Atomic Layer Deposition: Authors, Topics, and Collaborations. *PLOS ONE* **2018** *13*, e0189137.
[4] Caskey, C. M., et al. Semiconducting Properties of Spinel Tin Nitride and Other IV_3N_4 Polymorphs. *J. Mater. Chem. C* **2015**, *3*, 1389–96.
[5] Stewart, D. M., et al. Tin Oxynitride Anodes by Atomic Layer Deposition for Solid-State Batteries. *Chem. Mater.* **2018**, *30*, 2526–34.
[6] Du, Li., et al. The First Atomic Layer Deposition Process for Fe_xN Films. *Chem. Comm.* **2019,** *55,* 1943*1946.
[7] Burton, B. B., et al. Tantalum Nitride Atomic Layer Deposition Using (Tert-Butylimido)Tris(Diethylamido)Tantalum and Hydrazine. *J. Electrochem. Soc.* **2008**, *155*, D508-D516.
[8] Abdulagatov, A. I., et al. Atomic Layer Deposition of Aluminum Nitride Using Tris(Diethylamido)Aluminum and Hydrazine or Ammonia. *Russian Microelectronics* **2018**, *47*, 118–30.
[9] Elam, J. W., et al., Atomic Layer Deposition of Tin Oxide Films Using Tetrakis(Dimethylamino) Tin. *J. Vac. Sci. Tech. A,* **2008**, *26*, 244-252.
[10] Choi, D.-w., et al. The Conducting Tin Oxide Thin Films Deposited via Atomic Layer Deposition Using Tetrakis-Dimethylamino Tin and Peroxide for Transparent Flexible Electronics. *Appl. Surf. Sci.*, **2014**, *6*, 585-590.

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