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# Investigating a Few Remaining Unknowns of Reactive Multilayers affecting Ignition and Self-Propagating Reactions

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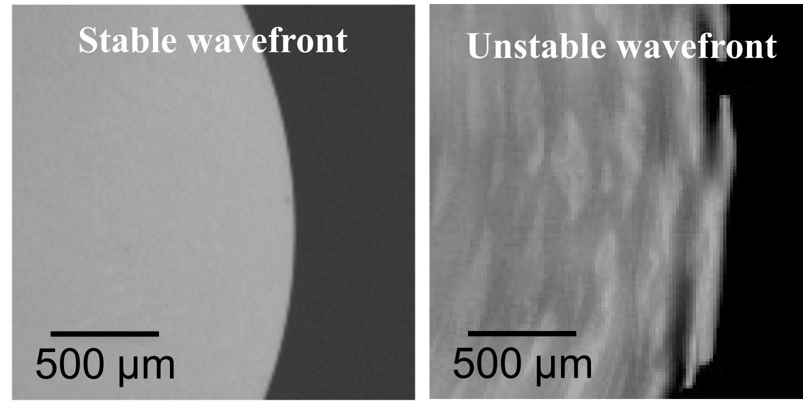
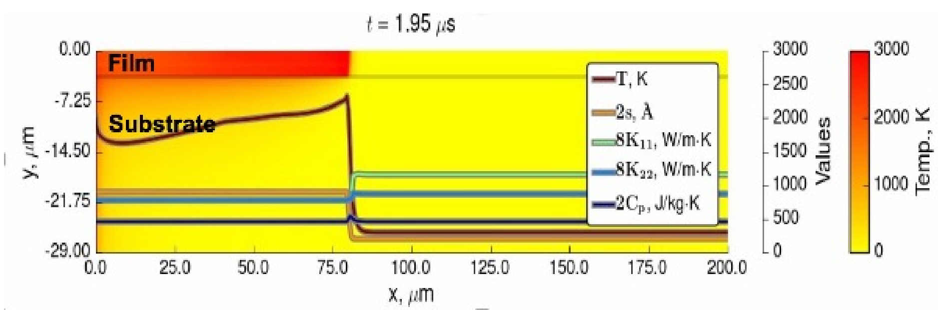
# Reactive films and blanket coatings are of interest for several applications.

*Wavefront stability is important to reliable use*

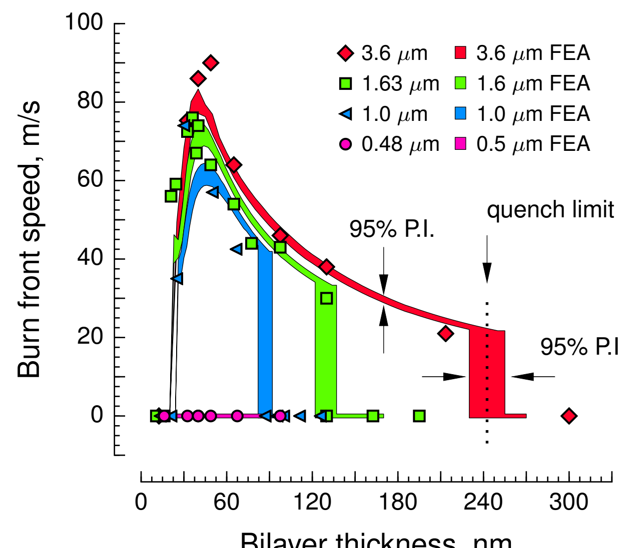



Joining by soldering (~10s of μm)

Heat sources for energy (~10s μm)




*Finite Element Simulations of Al/Pt reacting on substrate: David Kittell (Sandia)*



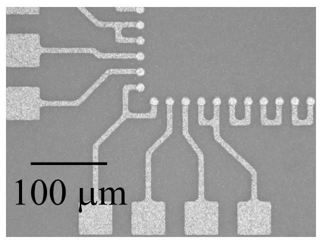
# Processing presents numerous alternatives for design but with associated challenges.

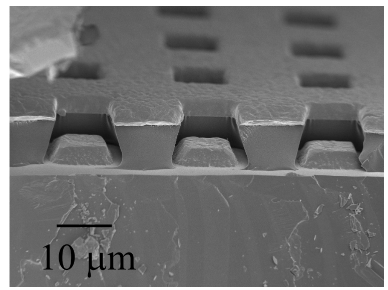
**Physical vapor deposition**

$10^{-9}$ - $10^{-7}$ Torr base pressure
> 99 % uniformity across 6” dia.
Maintain low temperature
Precision: ~1 nm
Various materials

**Photolithography**

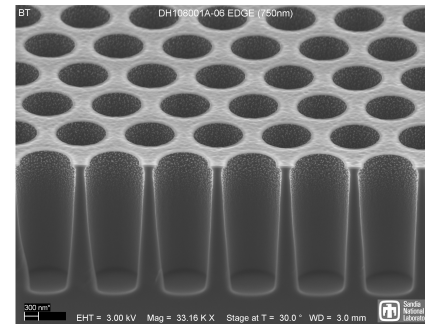
Feature definition by liftoff




**Bosch etching**

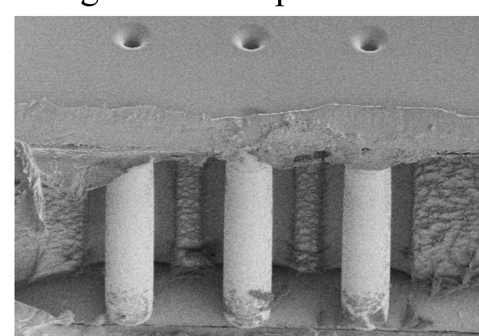
Etching submicron features in Si
High aspect ratios



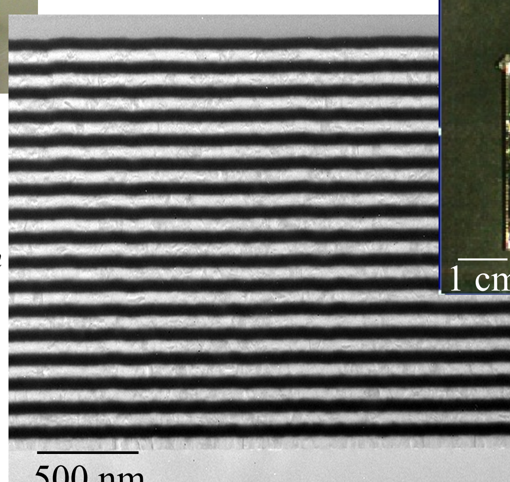
Cross Section showing partially etched holes, Ø = 1 micron

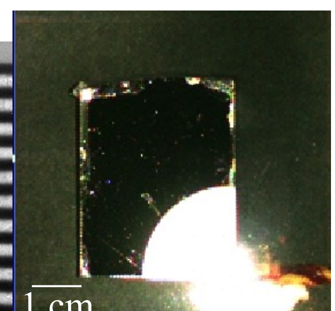
**Atomic layer deposition**

Infiltration (few materials)
Conformal coatings
Angstrom level precision



*Reactive multilayer shown by TEM in cross section*



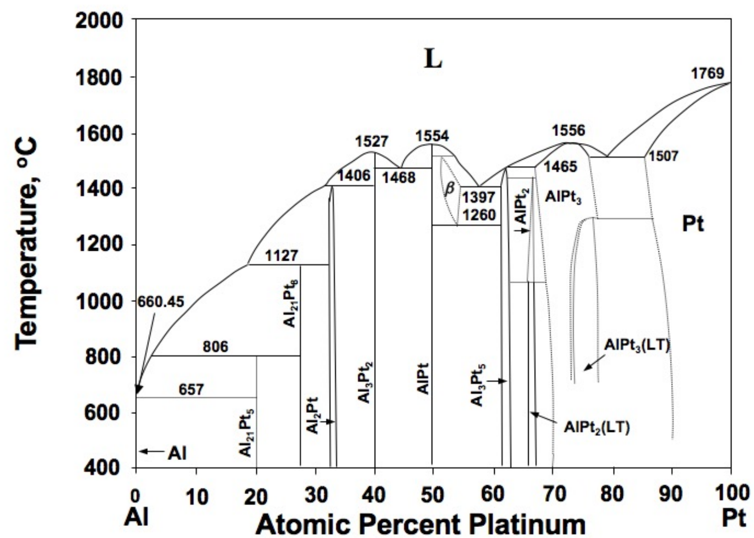
# Outline

i) A look at reactive properties across the full range of stoichiometry for the Al/Pt system

- Heats ($\Delta H_{rxn}$, $\Delta H_{Al_xPt_y}$)
- Ignition (experiments, analytical model)
- Wave speeds (experiments, analytical model)

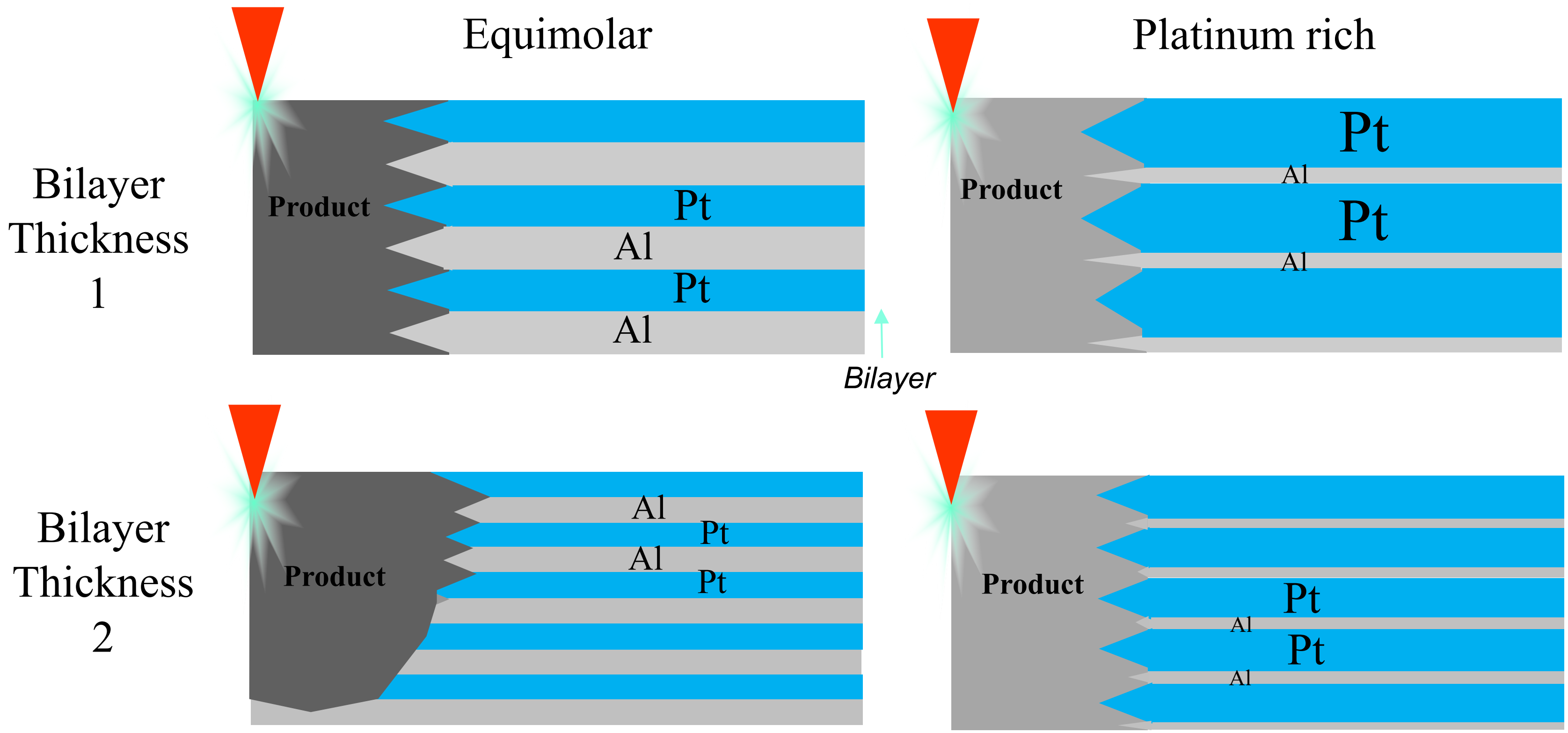
ii) Investigations of thermal conductivity by Time Domain Thermoreflectance (TDTR)

- Variation with bilayer thickness
- Changes with chemistry (Al/Pt, Co/Al, NiV/Al)



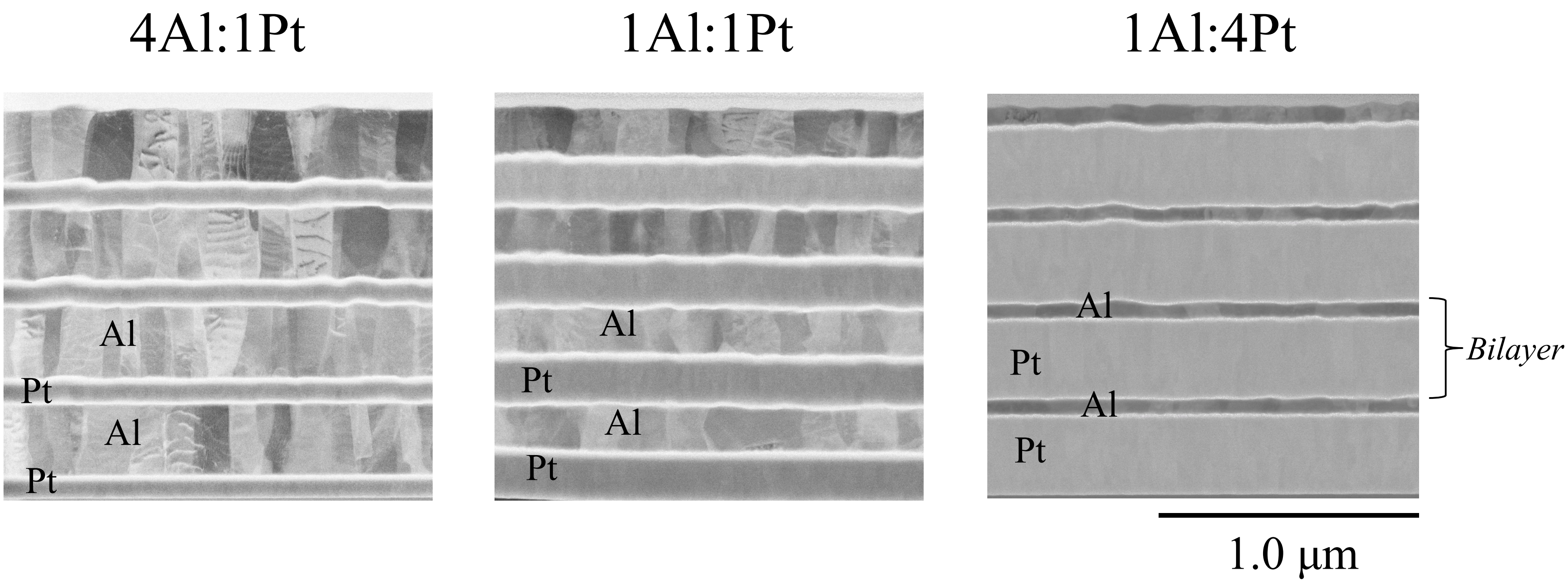

Phase Diagram redrawn from McAlister and Kahan, ASM 1986

# Multilayers have been made with different overall stoichiometry and periodicity.




Stoichiometry varied from 9Al:1Pt to 1Al:9Pt.
Bilayer thickness varied from 10 nm to 1600 nm.
Total multilayer thickness fixed at 1.6 µm.

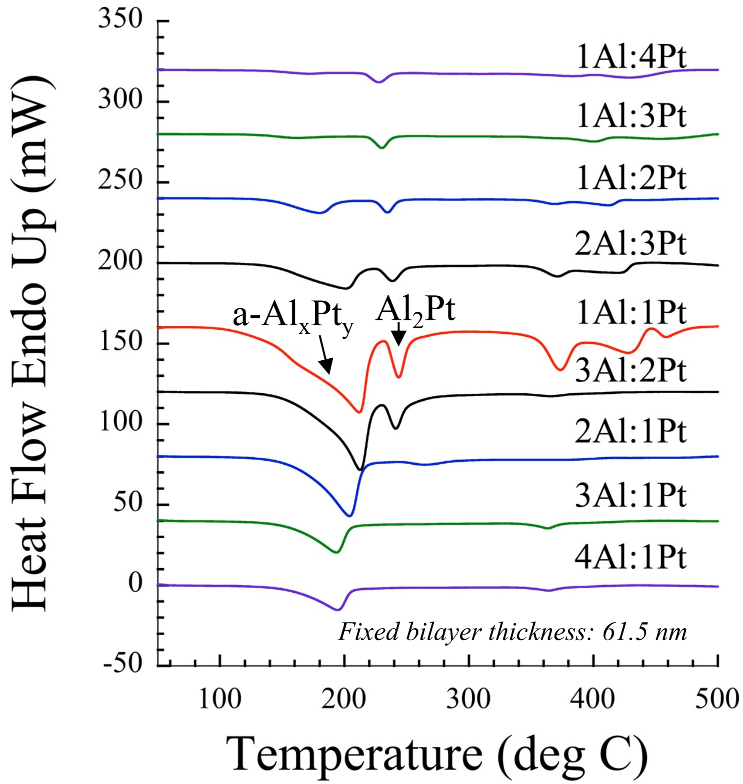
# Example multilayers are shown by SEM.




*Each has a bilayer thickness of ~400 nm.*

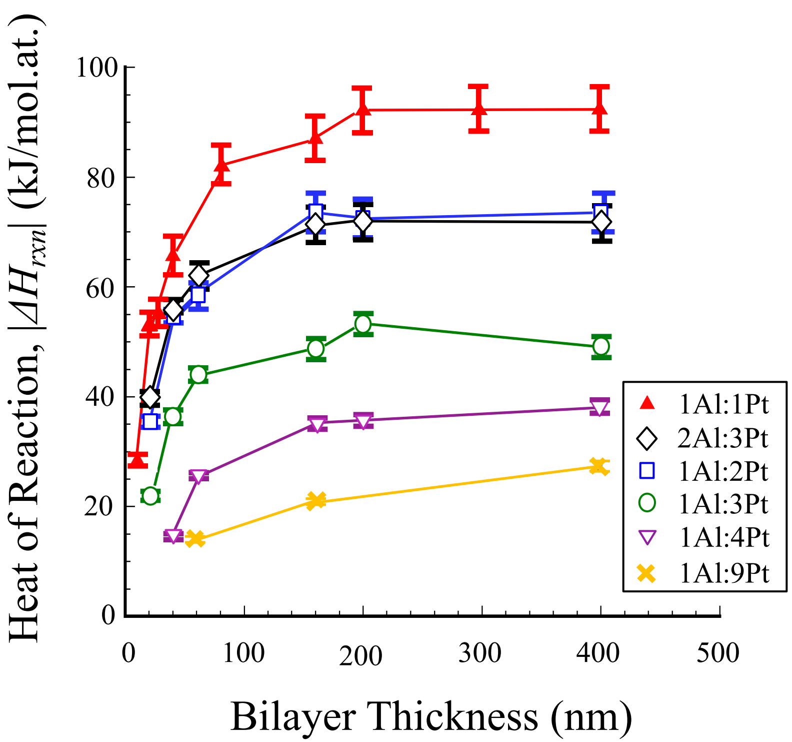
# Differential Scanning Calorimetry is used to obtain thermograms from Al/Pt.

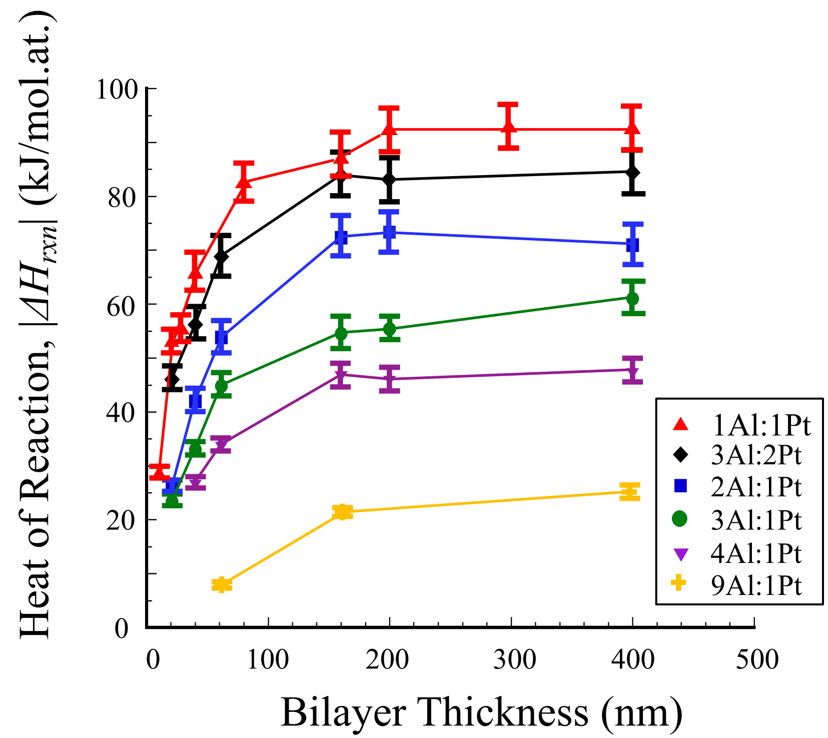
- All $Al_xPt_y$ stoichiometries studied here are characterized by exothermic reactions.
- First exotherms starts at ~100$^o$C.
  - Separate XRD confirms growth of amorphous interlayer (a-$Al_xPt_y$) is associated with first, broad exotherm.
- Additional exotherms
  - associated with formation of different crystalline intermetallic phases (many cases starts with $Al_2Pt$)




Heating rate: 40 degrees / minute
Gaseous environment: $N_2$
Perkin Elmer DSC system

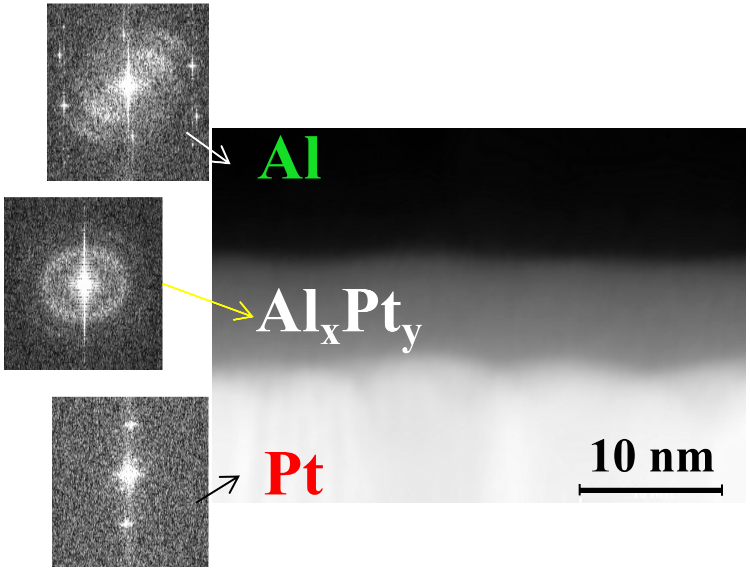
# Measured heats of reaction vary with bilayer thickness and stoichiometry.

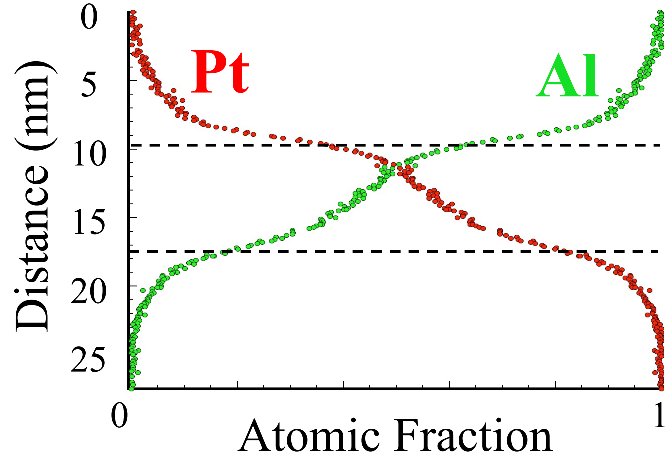


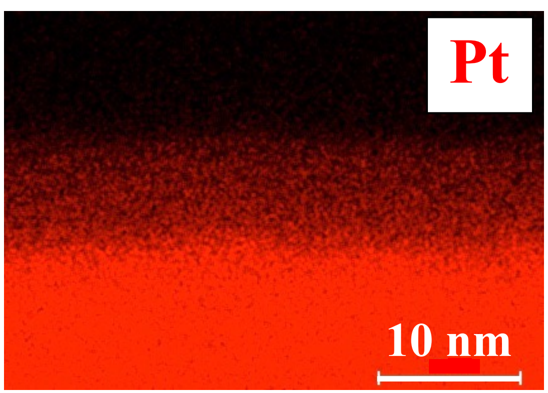



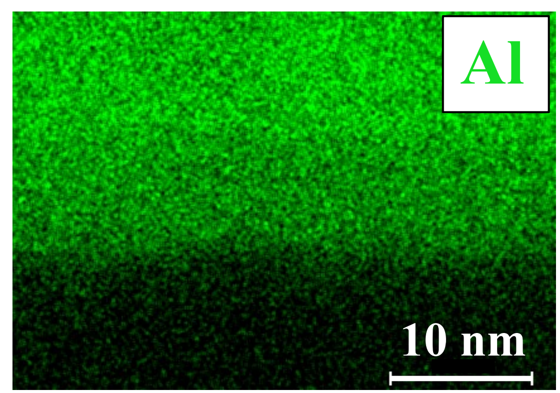

- Equimolar multilayers exhibit greatest $|\Delta H_{rxn}|$, when comparing multilayer of identical bilayer thickness.

# Interface structure and composition within an Al/Pt multilayer is revealed by TEM/EDS.

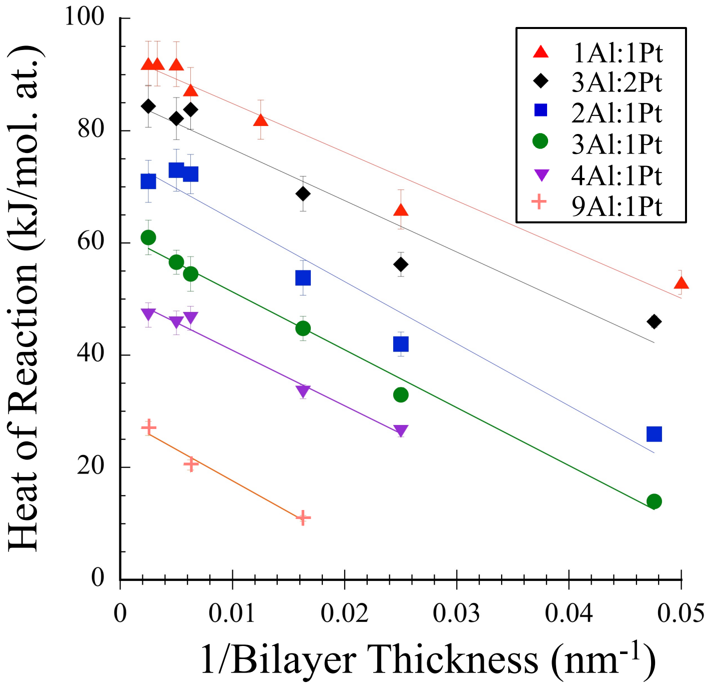


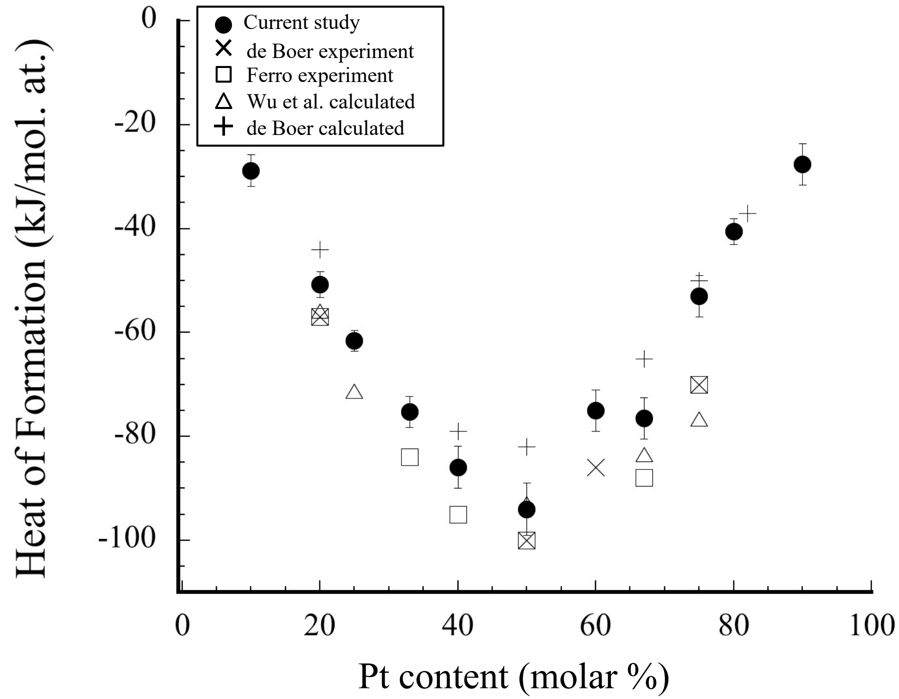



# Heats of formation are determined from measured heats of reaction.




$$\Delta H_{rxn} = \Delta H_{Al_xPt_y} - \Delta H_{premix}\left[\frac{2\,w\,V_{Al_xPt_y}}{t_B\;V_{premix}}\right]$$

**Measured Heat of Reaction**

**Heat of Formation**

**Amount lost via premixing**

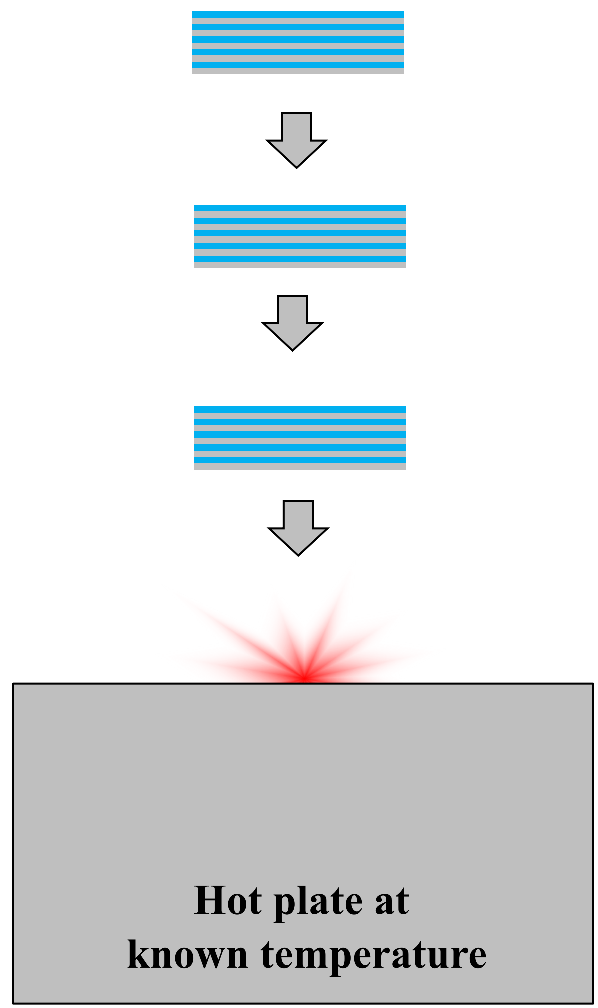
*w = premix thickness*

*$t_B$ = bilayer thickness*

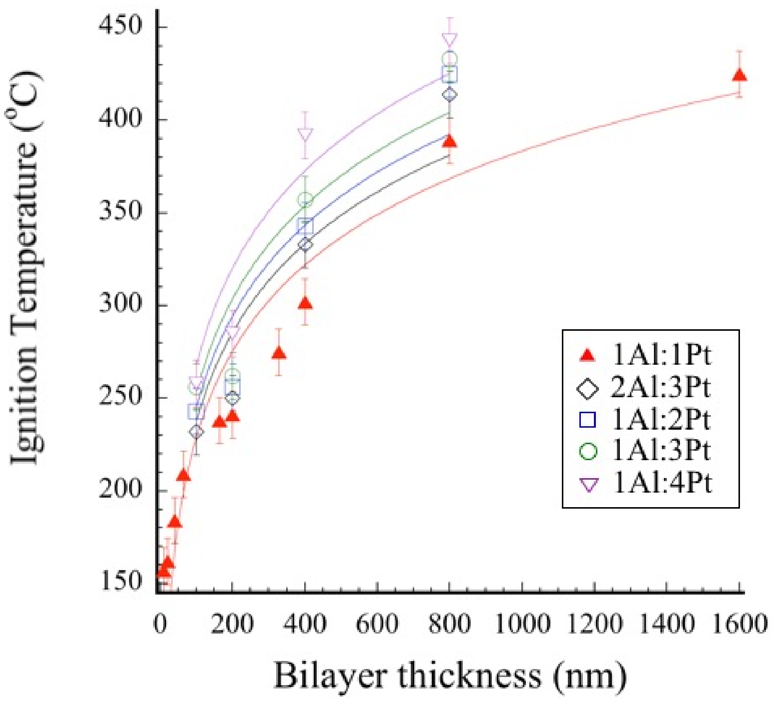
*V = molar atomic volume*

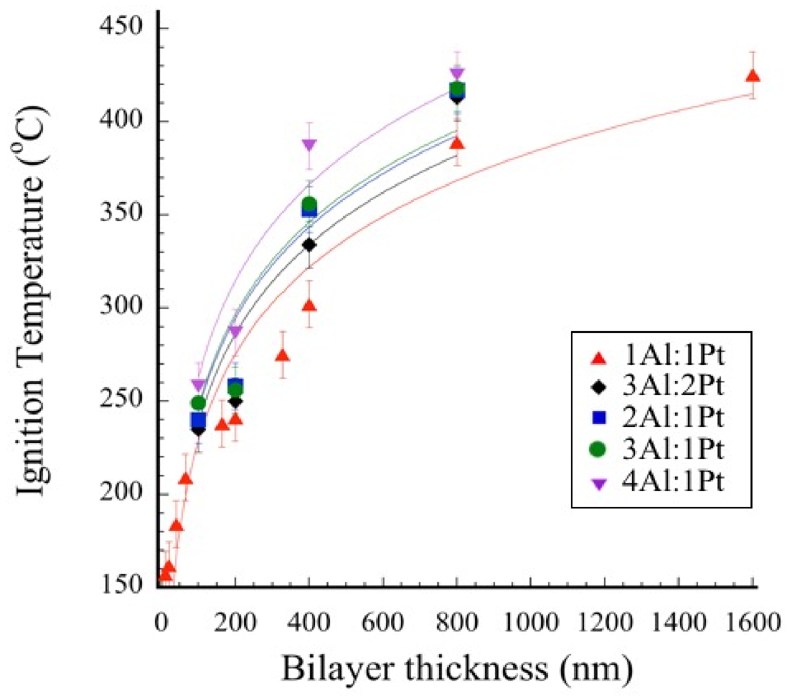
# Thermal ignition experiments

- Equilibrate hotplate at known temperature (in air)
- 1 $mm^2$ sample is tossed onto hotplate to contact on planar face
- Observed during contact to view one of two behaviors:
  - Ignition (evidenced by bright flash and burst into microscopic debris.
  - No ignition (subtle changes in shape, slight discoloration due to oxidation)



# Ignition temperature ($T_{ig}$) varies with bilayer thickness and stoichiometry.



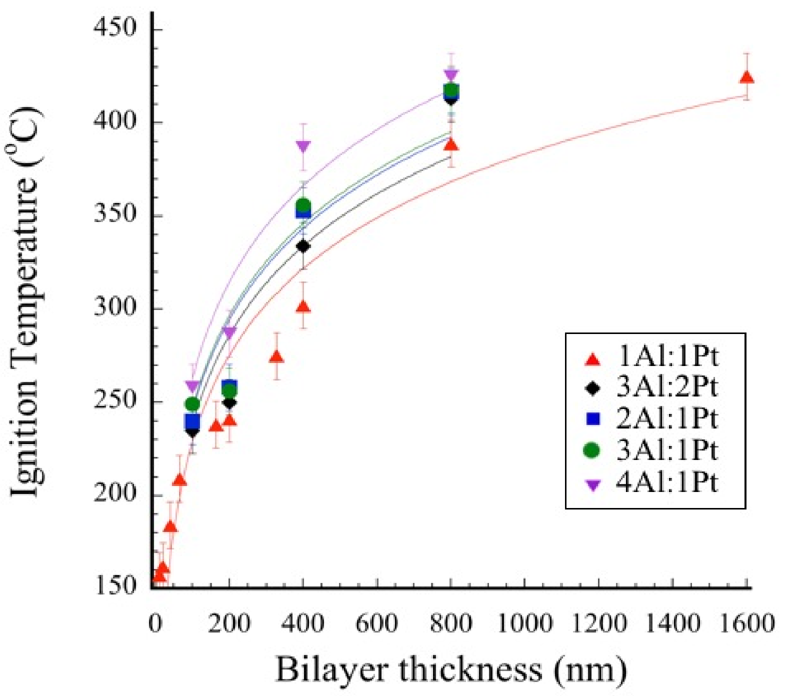




- Ignition temperature increases with bilayer thickness for each molar ratio.
- Equimolar multilayers exhibit lowest ignition temperatures.

# Logarithmic dependence of $T_{ig}$ with bilayer thickness for each stoichiometry.

Analytical expression* for ignition temperature:

$$T_{ig} = \frac{E_a / R}{ln\left[\left[\frac{2\ \tau\ \Delta H_{rxn}\ D_o\ R_T}{t_B\ w}\right]\frac{f}{n(1-n)}\right]}$$




*w = premix thickness*
$t_B$ = *bilayer thickness*
$\Delta H_{rxn}$ = *heat of reaction*
$R_T$ = *thermal resistivity*
$\tau$ = *thickness of multilayer*
$E_a$ = *activation energy*
*n = molar fraction*



*G.M. Fritz, S.J. Spey, Jr. M.D. Grapes, T.P. Weihs, J. Appl. Phys. 2013

# Activation energies associated with reactant mixing are estimated.

Analytical expression* for ignition temperature:

$$T_{ig} = \frac{E_a \;/ R}{ln\left[\left[\frac{2\ \tau\ \Delta H_{rxn}\ D_o\ R_T}{t_B\ w}\right]\frac{f}{n(1-n)}\right]}$$

*w* = *premix thickness*
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$R_T$ = *thermal resistivity*
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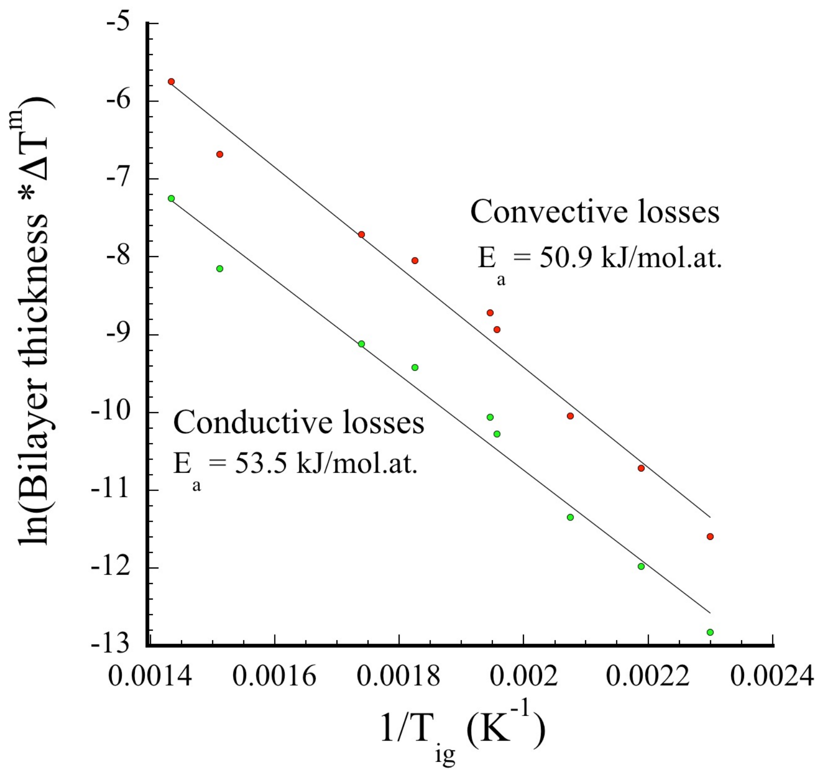
*n* = *molar fraction*




Activation energies attributed to the solid state diffusion of reactants.



*G.M. Fritz, S.J. Spey, Jr. M.D. Grapes, T.P. Weihs, J. Appl. Phys. 2013

# High speed videography of propagating waves is used to evaluate front morphology and speed.

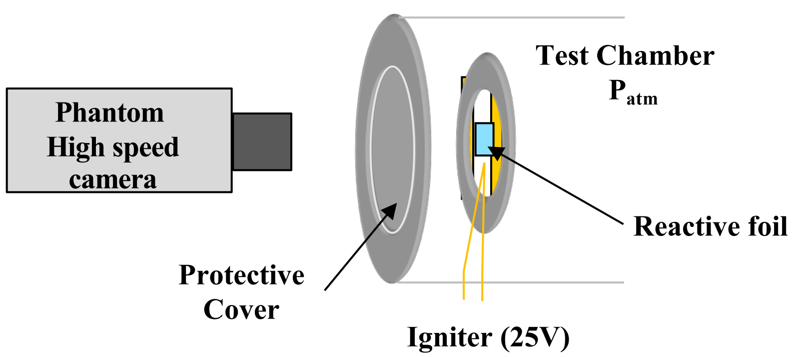
Tested as freestanding foils

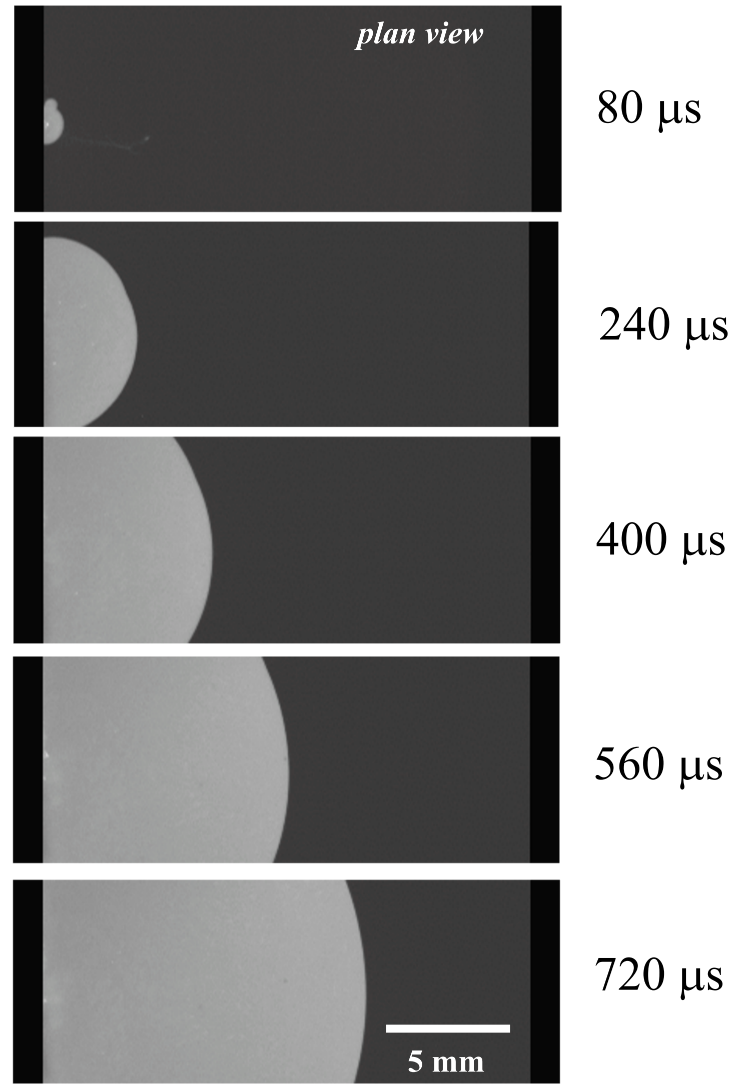
Point ignition in air

No preheat above room temperature

Evaluate front position: outside ignition zone

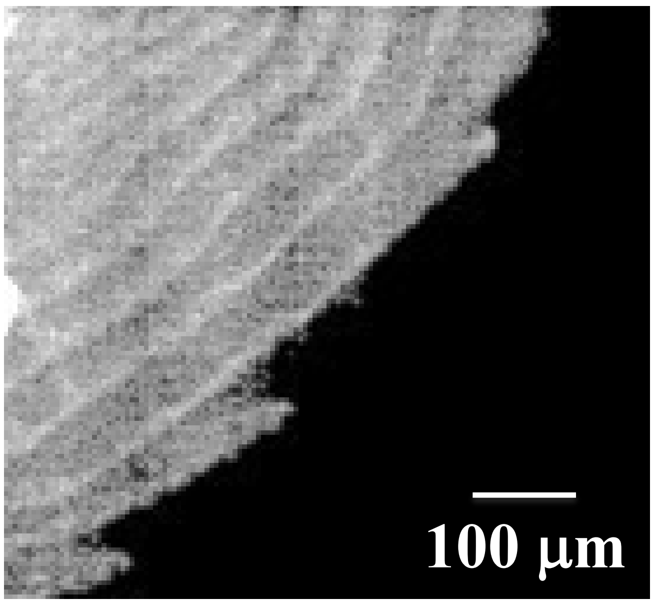
Position is plotted versus time to determine speed



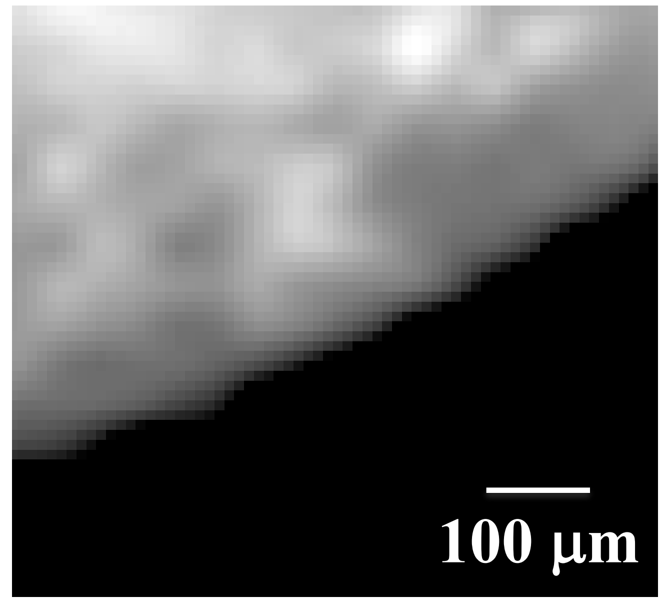




*Equiatomic Al/Pt, bilayer thickness: 50 nm*

# Most multilayers undergo stable propagation. Only one design, near a limit of stoichiometry, exhibited an instability.



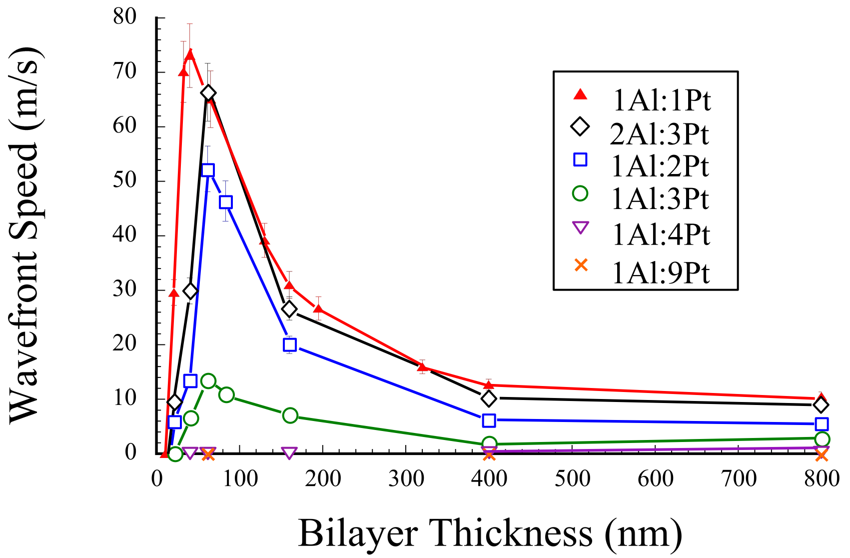

1 Al: 4 Pt
Bilayer thickness = 800 nm

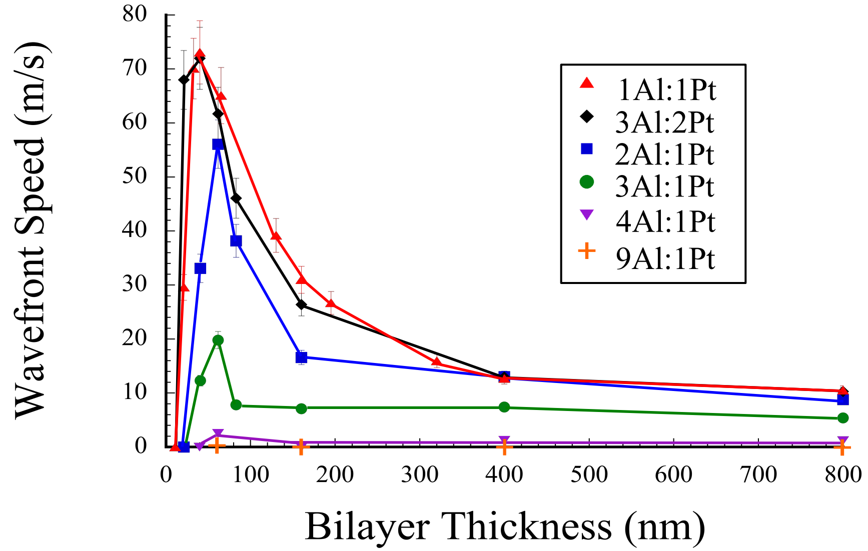



All other reactive designs,
(different molar ratios,
bilayer thicknesses)

Unstable modes predicted near concentration limits: A.S. Rogachev, F. Baras, et al. Doklady Physics 53 (2008).

# Wavefront speed varies with bilayer thickness and stoichiometry.




- Zero speed means multilayer could not be ignited (multiple attempts).
- The range of reactive stoichiometry spans 20 to 80 at.% Pt (including endpoints).

# Attempts to utilize the analytical model by Mann et al. to predict wavefront speeds.

$$v_{flame}^2 = \left( \sum_{n=odd} \frac{k_n^2}{\alpha_n^2} \right)^{-1} \frac{4A\,RT_{max}^2\,\lambda^2}{E(T_a - T_o)} \exp\left(-E/RT_{max}\right)$$

A = Arrhenius prefactor
R = gas constant
$\lambda$ = thermal diffusivity (in plane)

E = activation energy
$T_{max}$ = maximum temperature
$T_o$ = ambient temperature

$k_n$ = Fourier coefficients
$\alpha_n$ = Fourier eigenvalues
$T_a$ = adiabatic temperature

Eq. from A.B. Mann, A.J. Gavens, M.E. Reiss, D. Van Heerden, G. Bao, T.P. Weihs et al. J. Appl. Phys. 82 (1997).

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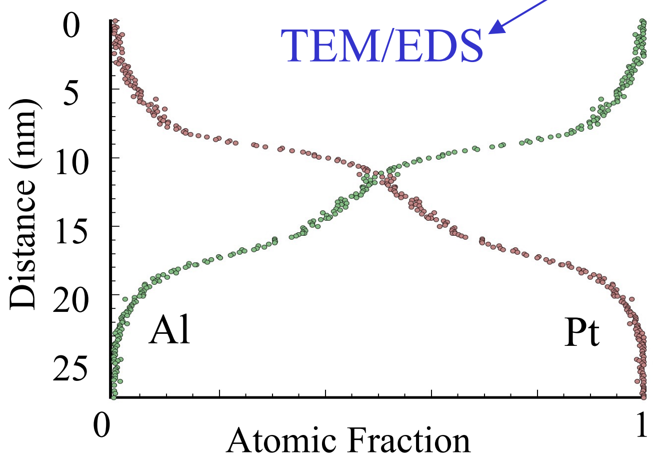
TEM/EDS



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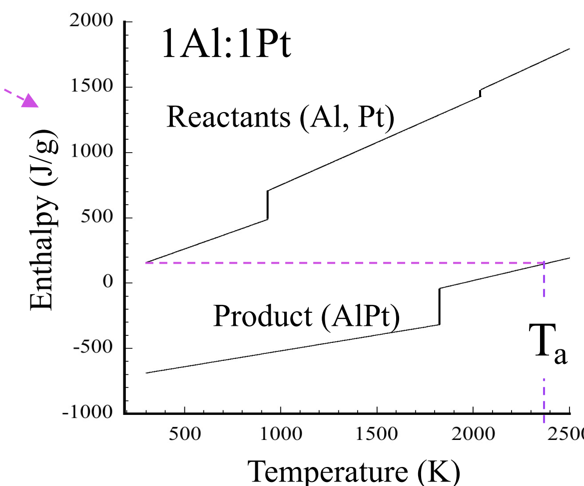
Enthalpy – Temp. Diagrams



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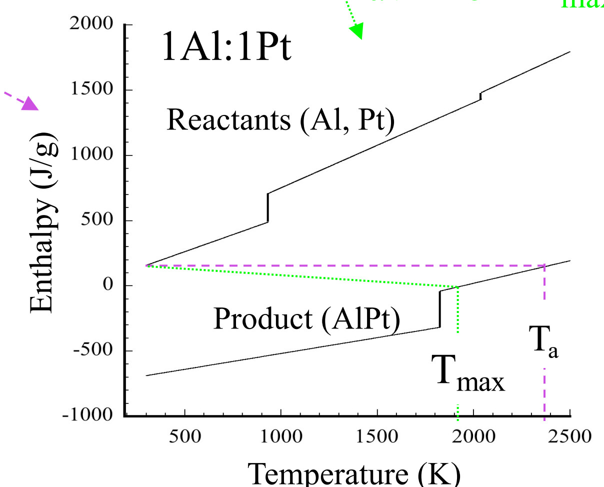
utilize $\Delta H_{max}$

Enthalpy – Temp. Diagrams



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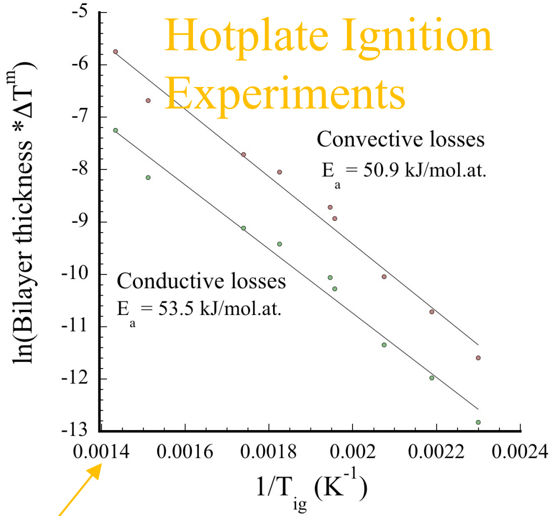


$$v_{flame}^2 = \left( \sum_{n=odd} \frac{k_n^2}{\alpha_n^2} \right)^{-1} \frac{4A\,RT_{max}^2\,\lambda^2}{E(T_a - T_o)} \exp(-E/RT_{max})$$

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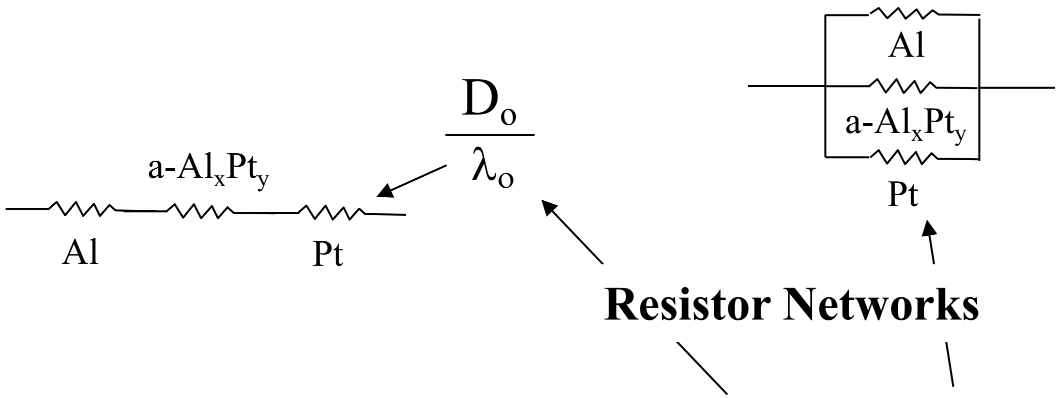


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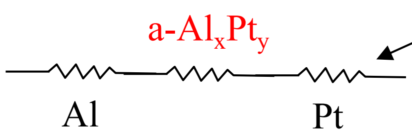
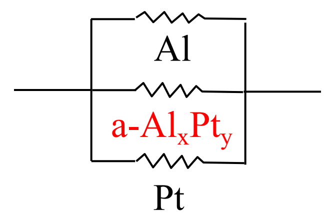
# Attempts to utilize the analytical model by Mann et al. to predict wavefront speeds.

Fitting parameters in RED

$$\frac{D_o}{\lambda_o}$$

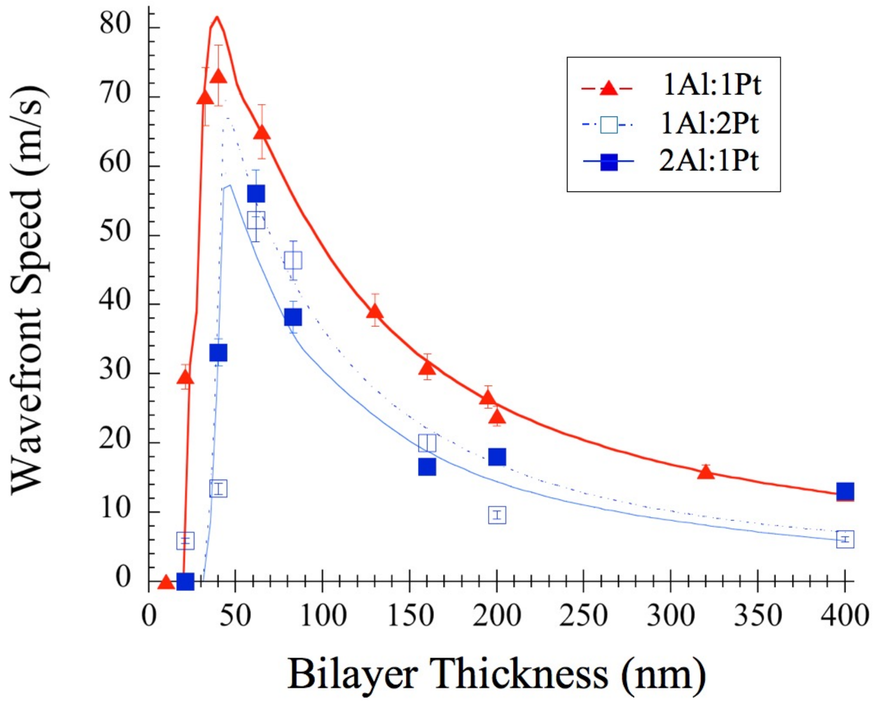


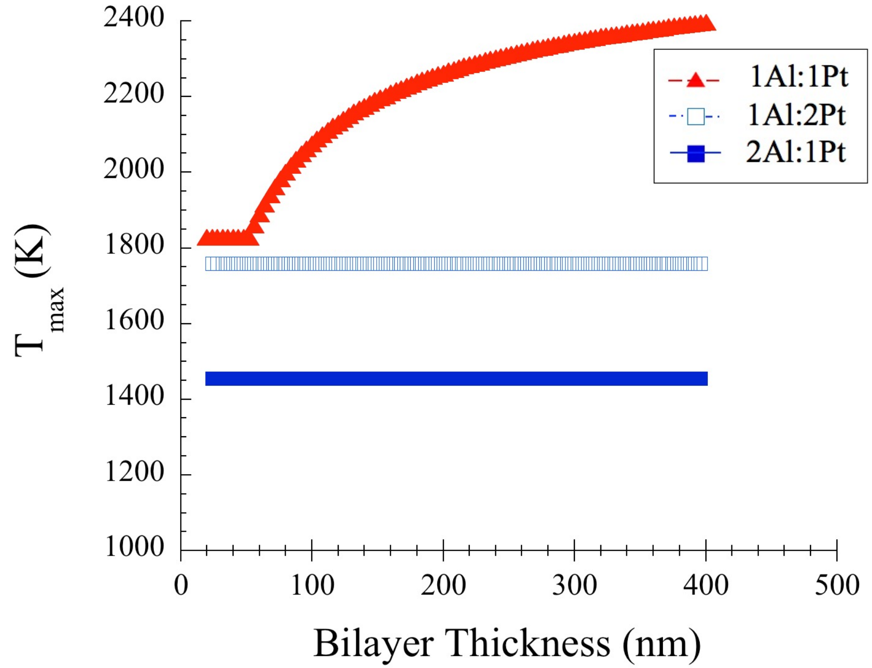




**Resistor Networks**

$$v_{flame}^2 = \left( \sum_{n=odd} \frac{k_n^2}{\alpha_n^2} \right)^{-1} \frac{4A\,RT_{max}^2\,\lambda^2}{E(T_a - T_o)} \exp(-E/RT_{max})$$

# Predicted propagation speeds match well to measured values (three stoichiometries).



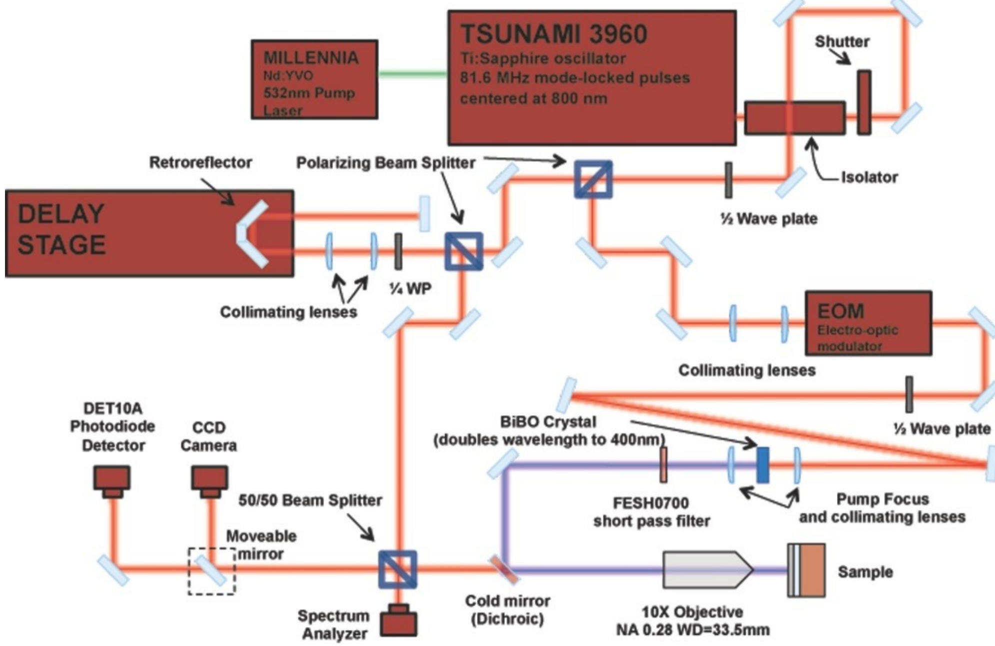



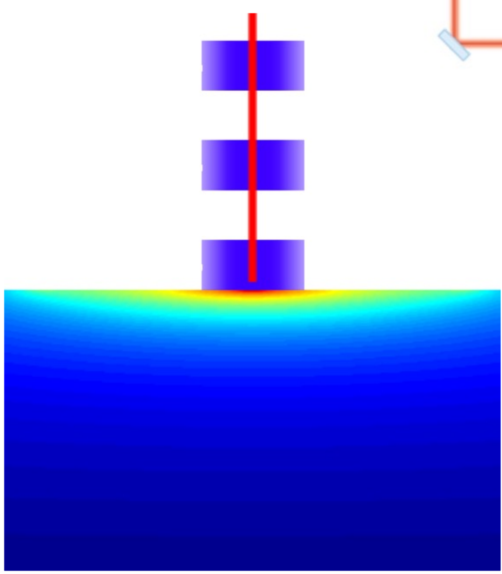

**Fit parameters (2):**

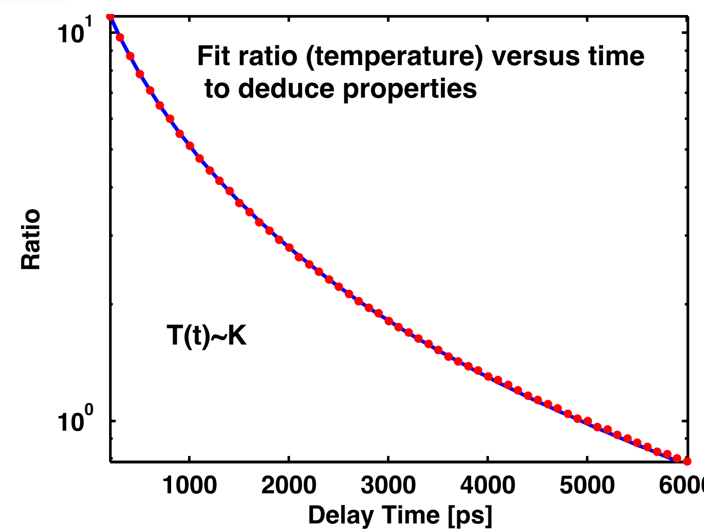
$D_o$ = 1.63 e$^{-6}$ m$^2$/s

$\lambda_{premix}$ = 2.8 e$^{-6}$ m$^2$/s (estimate k = 7 W/m·K)

# Time Domain ThermoReflectance (TDTR)
# for determining cross-plane thermal conductivity



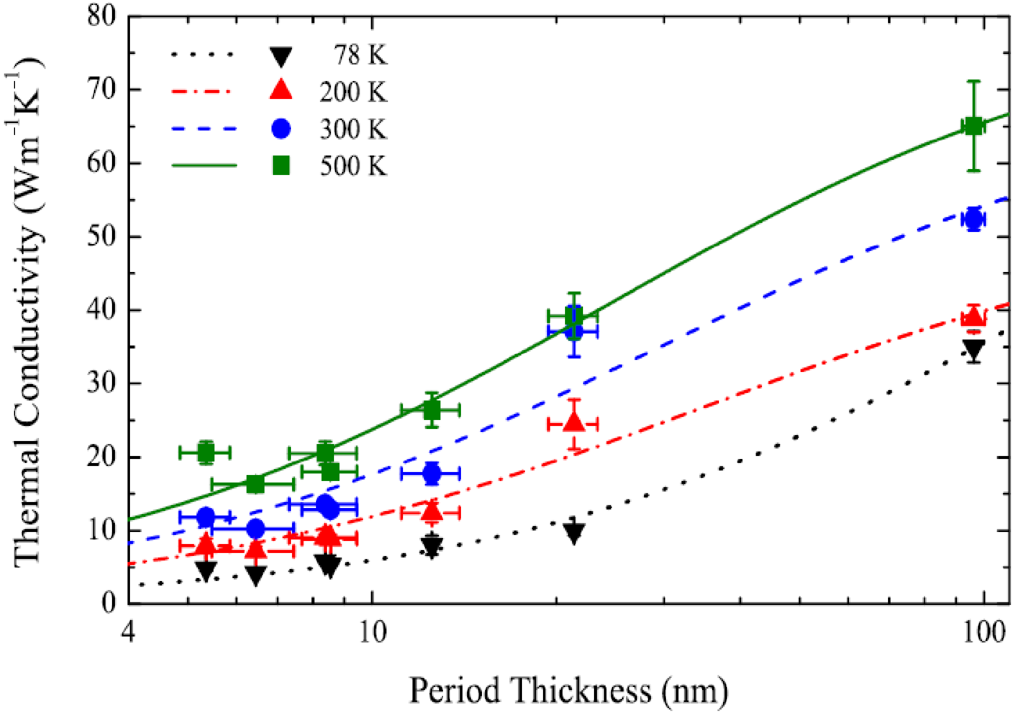





# TDTR has been used previously to determine thermal conductivity of thin film multilayers.

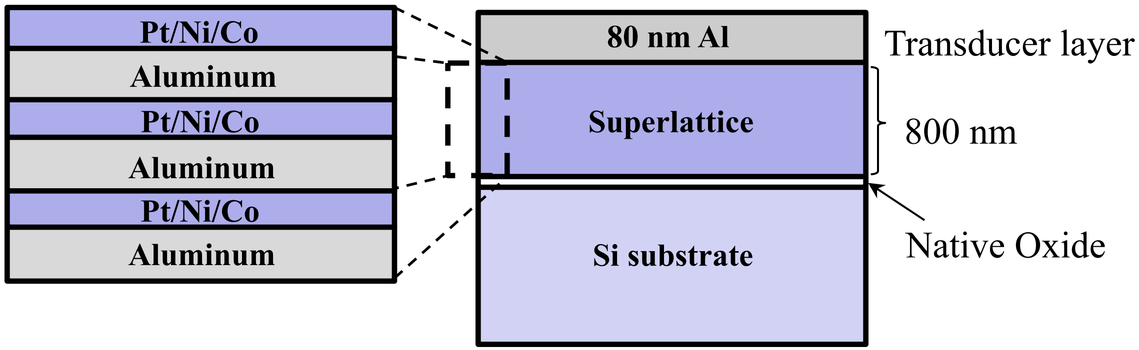
- Cu-Nb does not interdiffuse and so creates "perfect" interfaces.
- Metal multilayers found to obey lumped series resistance model

$$R_{tot} = \frac{d}{\kappa_{measured}} = R_0 + \frac{n}{h_{Cu-Nb}}$$

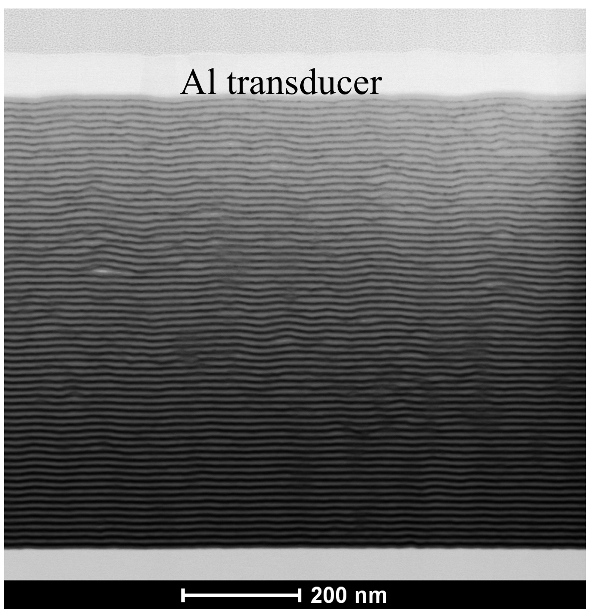



R. Cheaito, K. Hattar, J.T. Gaskins, A.K. Yadav, J.C. Duda, T.E Beechem, J.F. Ihlefeld, E.S. Piekos, J.K. Baldwin, A. Misra, P.E. Hopkins, *Applied Physics Letters,* **2015**, *106*, 093114

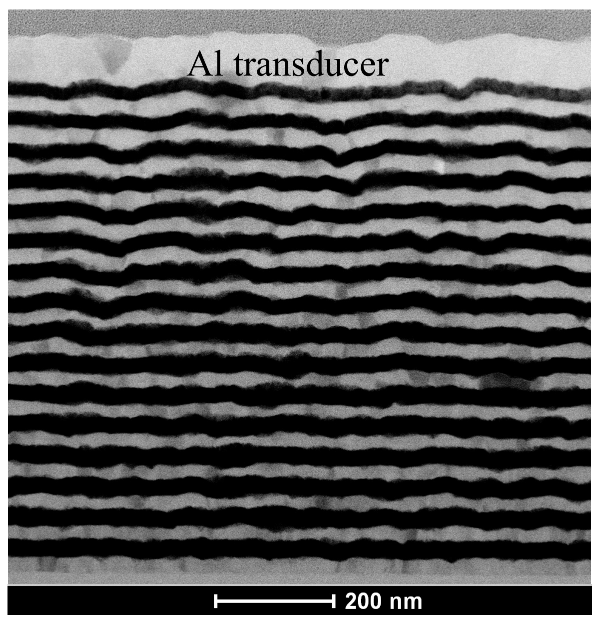
# Thin film test structures for TDTR



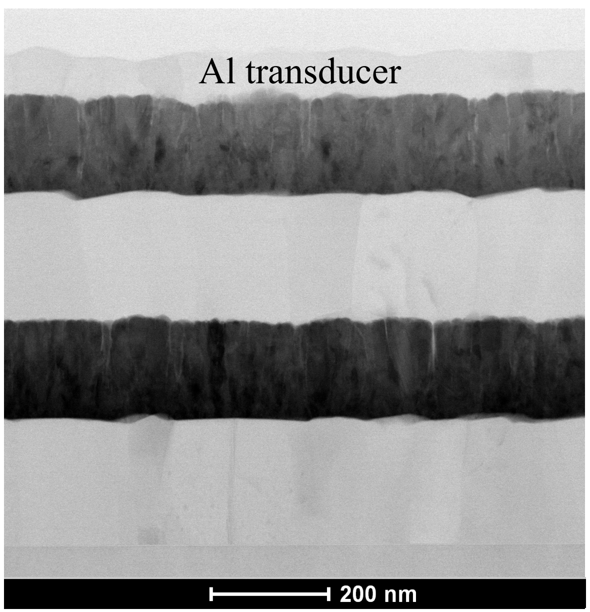

Small $t_B$



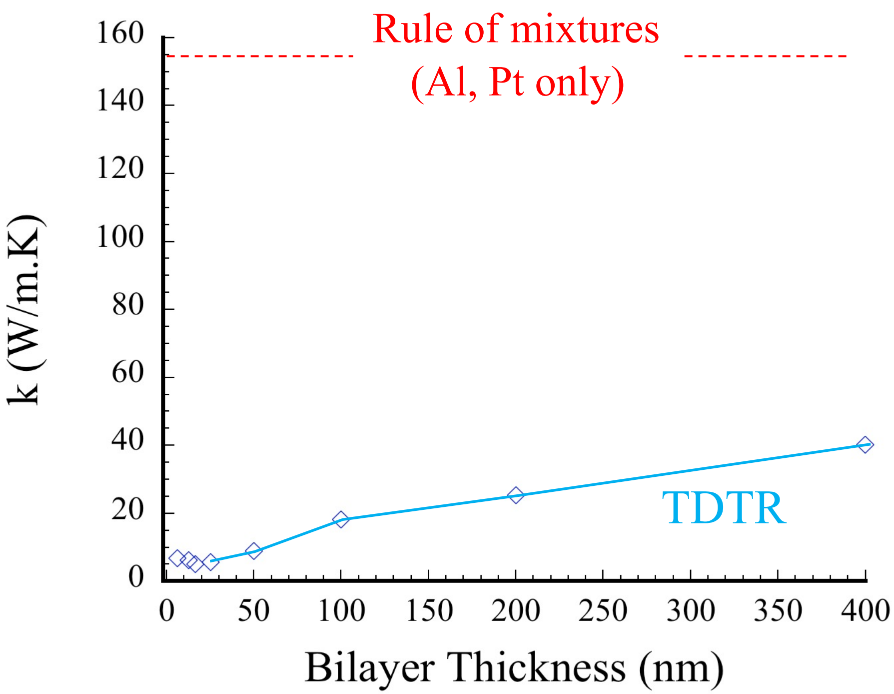

Medium $t_B$




Large $t_B$

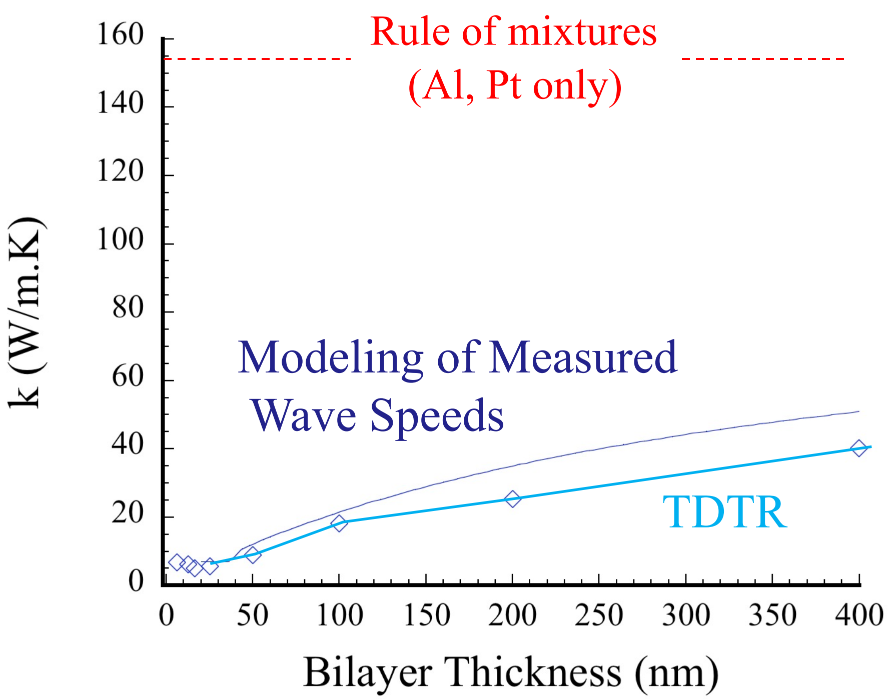


# Measured cross-plane thermal conductivity



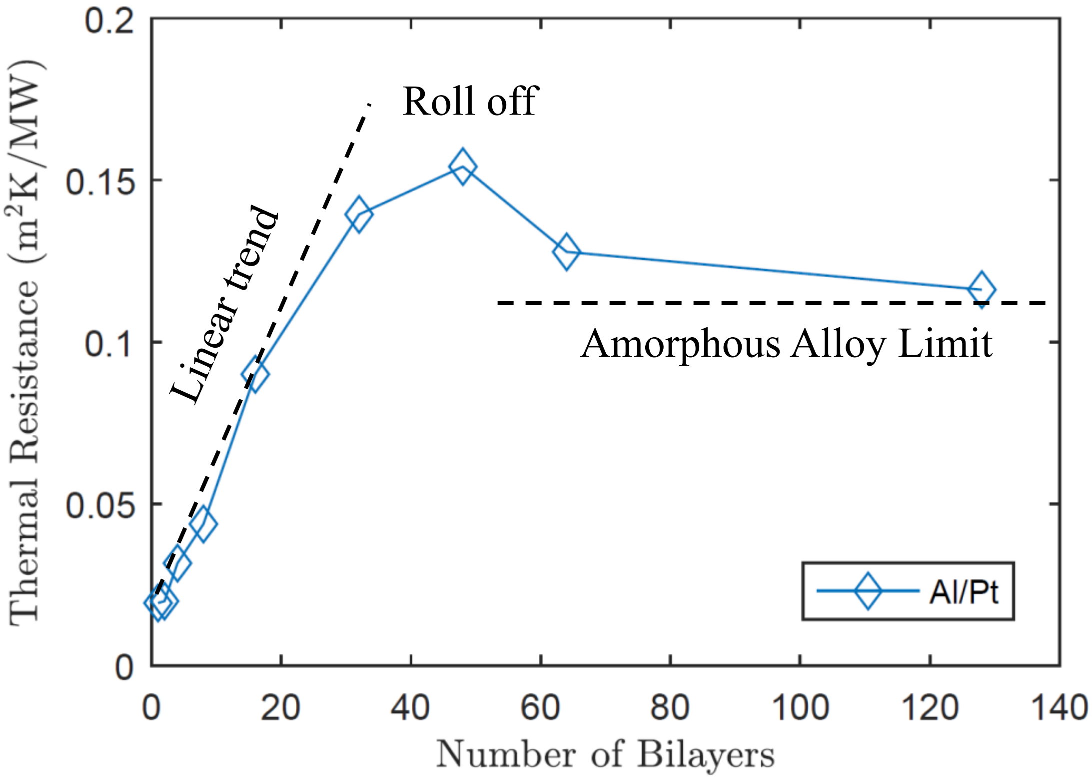

- Far below the rule – of – mixtures estimate
  - 154 W/m·K
- k varies with bilayer thickness
- Similar trend and values predicted for series resistor network used in velocity modeling.

# Measured cross-plane thermal conductivity




- Far below the rule – of – mixtures estimate
  - 154 W/m·K
- k varies with bilayer thickness
- Similar trend and values predicted for series resistor network used in velocity modeling.

# Does the series resistance model work?

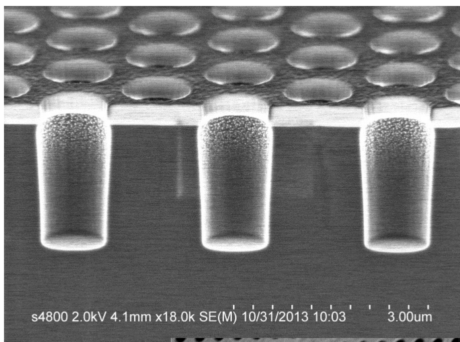


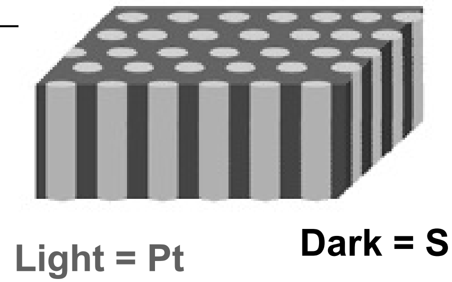

- Strong linear trend indicates model behavior
- Roll off indicates coherent transition
- Maximum resistance of metal multilayer greater than amorphous analogue

Detailed discussion of thermal can continue at a Poster tonight (ES09.03.36 Beechem, Saltonstall, Abere, Adams)

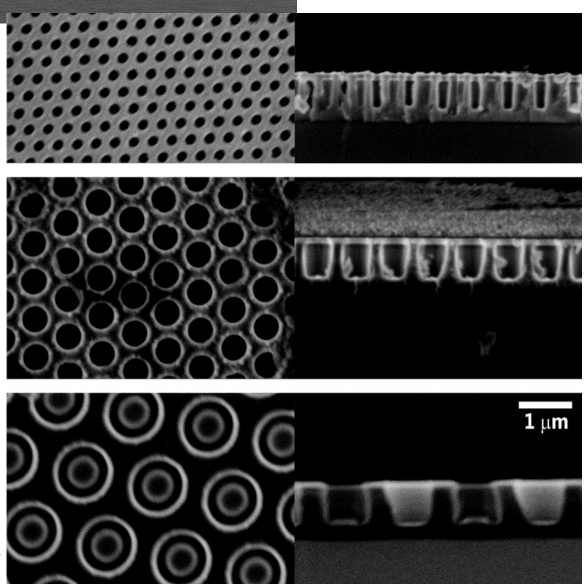
# Future direction: 2-D periodic reactive coatings fabricated by Bosch etching and ALD.

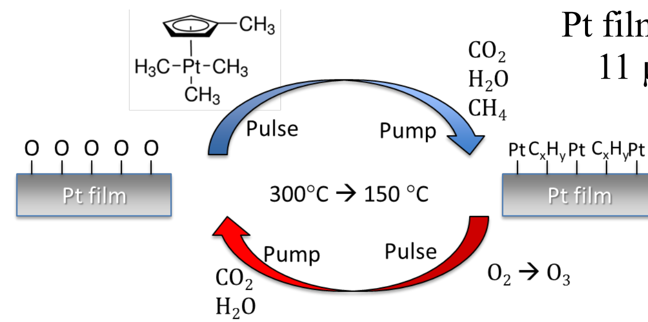
Cross Section showing partially etched holes, Ø = 1 μm








Pt film resistivity: 11 μOhm-cm

**Pt CVD - reaction:**

$$(MeCp)Pt(Me)_3(g) + O_3(g) \rightarrow Pt(s) + CO_{2(g)} + H_{2(g)} + CH_{4(g)}$$

**Pt-ALD - half-reactions: (150°C ~0.5 Å/cycle)**

$$Pt\text{-}O^* + (MeCp)Pt(Me)_3(g) \rightarrow Pt\text{-}(CH_3)_x^* + CO_{2(g)} + H_{2(g)} + CH_{4(g)}$$

$$Pt\text{-}(CH_3)_x^* + 3O_3(g) \rightarrow Pt\text{-}O^* + 3CO_2(g) + 3H_2O(g)$$

D.P. Adams, 10/17

# Summary

- Various techniques used for thin film fabrication and surface engineering provide the necessary control of stoichiometry, purity and dimension for detailed studies of structure-composition-property relationships in reactive materials.

- The range of reactive stoichiometry for bimetallic multilayers is large when periodicity is made small (nm scale)
  - Al/Pt: reactive designs span at least 20 to 80 at.% Pt.
  - Attributed to a substantial heat of formation and $T_a$ across molar range

- Heats, ignition temperatures and wavefront speeds vary with stoichiometry

- Past analytical models have been used to predict wavefront speeds for different stoichiometries that match experimental measurements.

- Thermal conductivity (cross plane) varies with bilayer thickness, overall chemistry and possibly the characteristics of the premixed zone.