Characterization of the chemical signal created by CO oxidation on Pt/GaN nanodiodes

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GaN deposition – Dan Koleske

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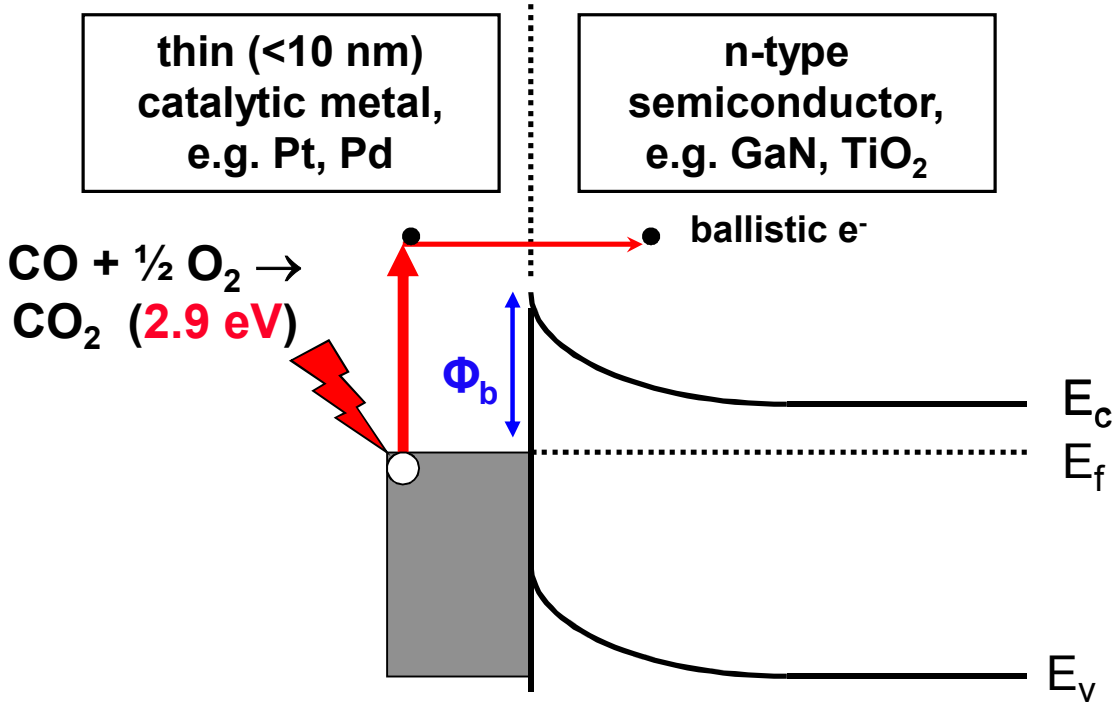
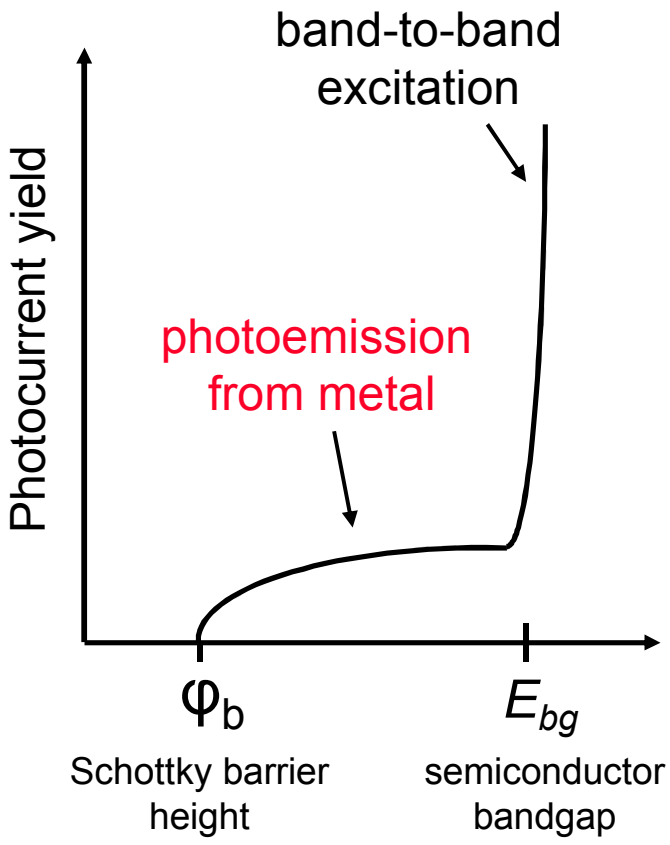
What is a "Catalytic Nanodiode"?

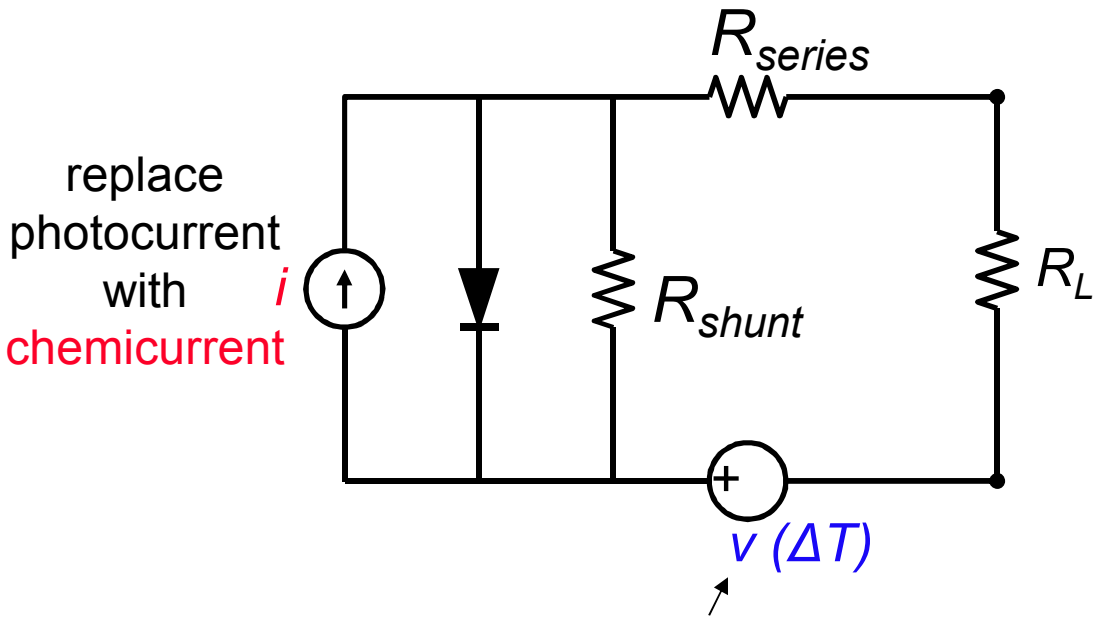
- **The catalytic nanodiode is a simple Schottky diode that converts chemical energy directly into electrical energy, via electronic excitation, i.e. hot electrons**
- **Somorjai et al. reported (2005) a reaction quantum yield (electrons/CO_2) up to ~75% for the CO oxidation reaction on Pt/TiO_2, coined the term "catalytic nanodiode"**



Best analogy to catalytic nanodiode is a Schottky diode solar cell or photodiode with sub-bandgap illumination



equivalent circuit



thermoelectric voltage,
typically 0.3-1.0 mV
before reaction conditions

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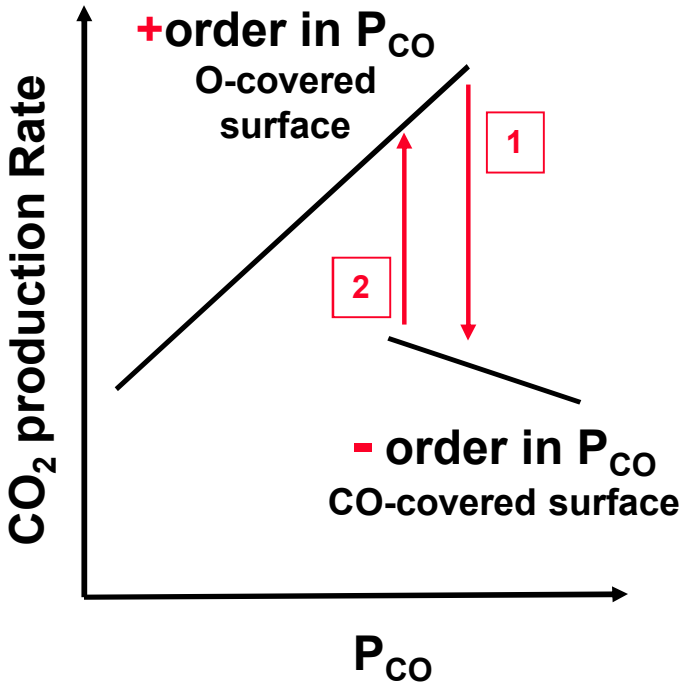
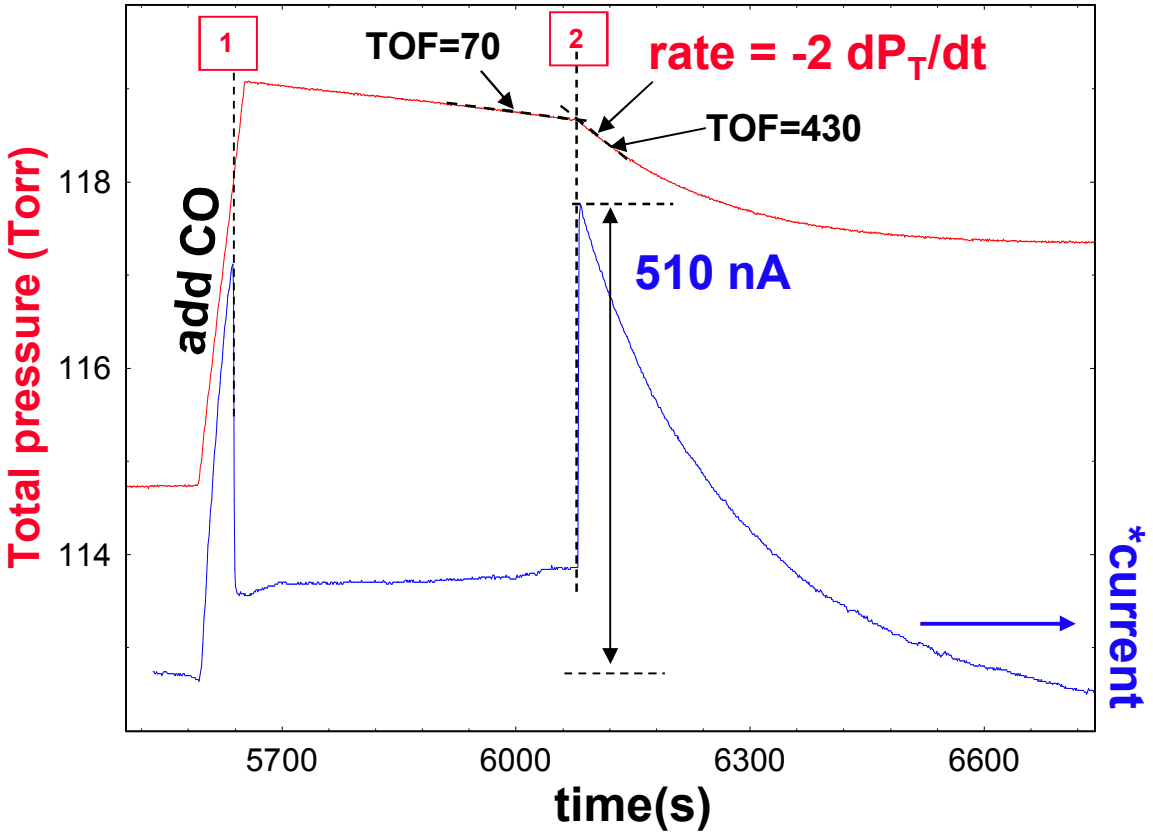
Kinetic phase transition during CO oxidation on Pt is observable using the nanodiode current



ref: e.g. Creighton JPC 1981

5 nm Pt/GaN nanodiode, 270°C



we use this lineshape as a fingerprint

* using solar cell convention for chemicurrent

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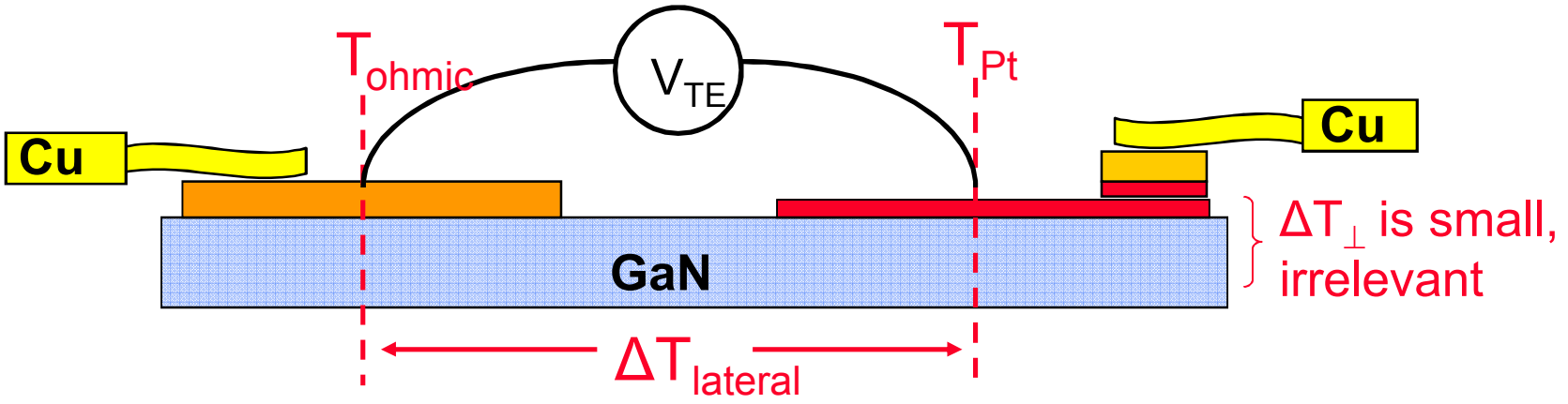
Is the electronic signal due to "chemicurrent" or is it derived from a voltage source?



$$V_{TE} \sim (S_{GaN} - S_{Cu})\Delta T_{lat} + \text{much smaller terms}$$

V_{TE} is mostly determined by:

1) GaN Seebeck coefficient; S_{GaN} [typically ~ -400 μV/deg]

2) the lateral temperature difference, ΔT_{lat}

only need ΔT_{lat} ~1°C

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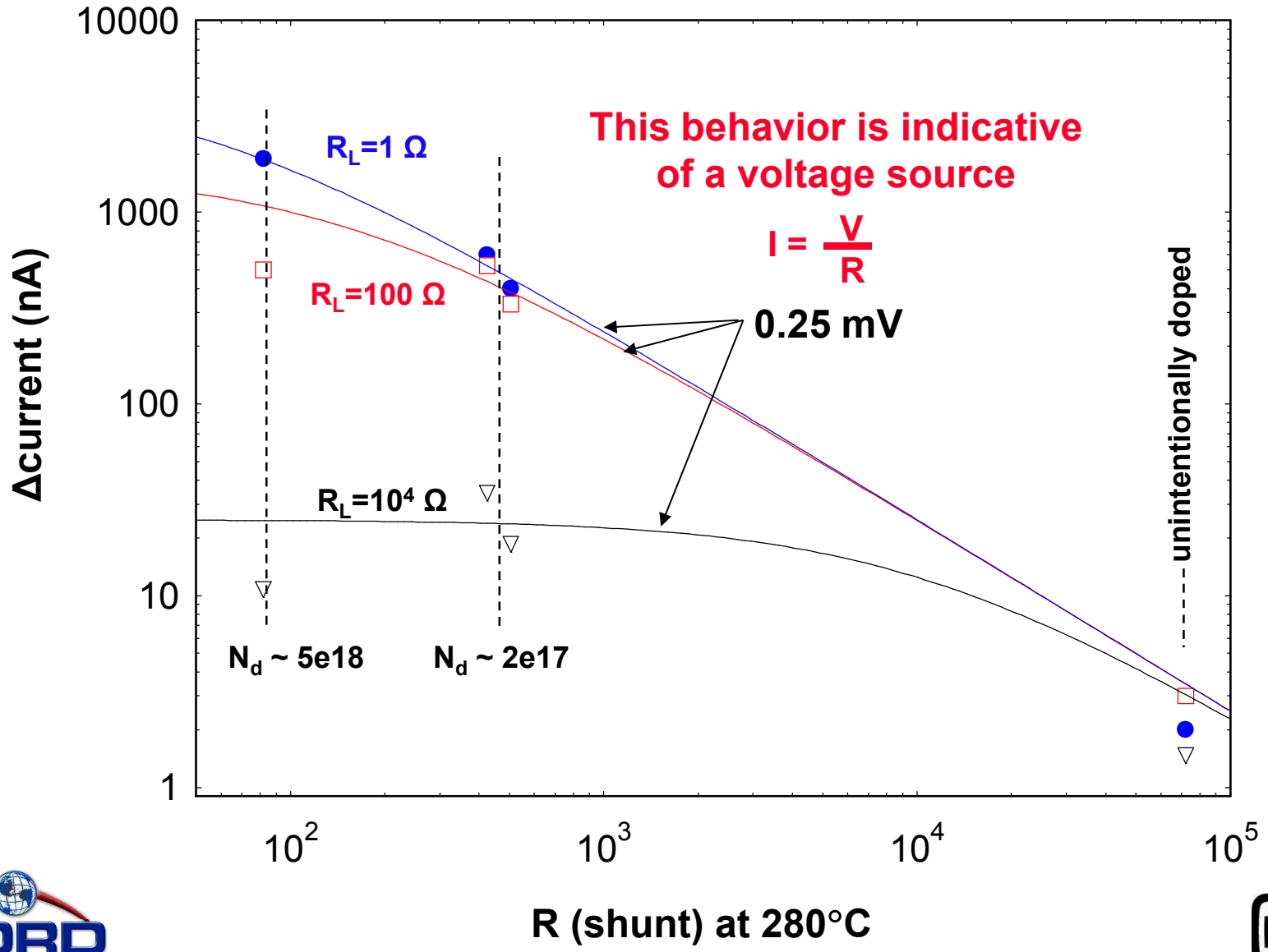
Vary R_{shunt} by varying GaN doping level



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The 2 Burning Questions

What is the magnitude of the Pt temperature rise, ΔT_{Pt}, during reaction?

How much is the lateral temperature gradient, ΔT_{lat}, affected by the reaction?

Reaction is exothermic; 68 kcal/mole, ~2.9eV/CO_2

For reaction TOF = 400, power density is 300 mW/cm^2

For reference: heater is dissipating 700 mW/cm^2 at 270°C

The heat liberated only needs to increase ΔT_{lat} by ~1°C in order to generate the measured signals

We use both theoretical and experimental methods to address these 2 questions

Theoretical:

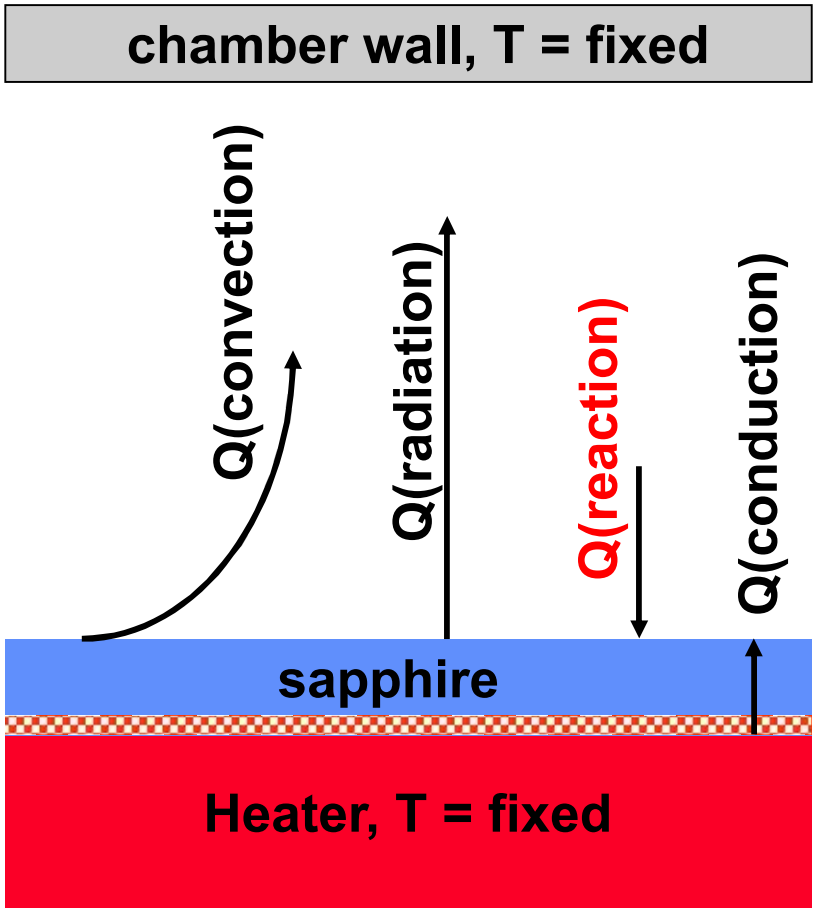
- "Simple" 1D and quasi-2D calculations
- Full 3D simulations of entire reactor

Experimental:

- mid-IR optical pyrometry of Pt surface: ΔT_{Pt}
- Thermocouple measurements of electrical contacts: ΔT_{lat}

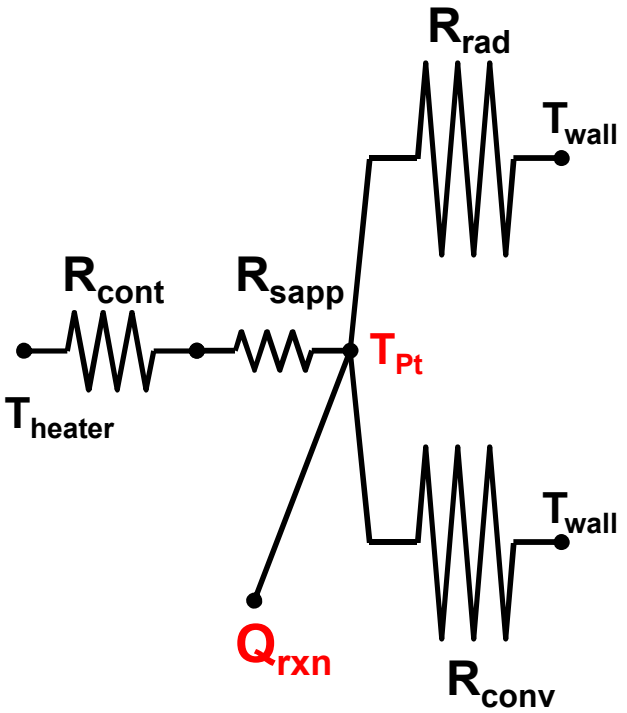
1D calculation with isothermal heater

Physical model



Equivalent thermal circuit

$$\Delta T = Q \cdot R_{thermal}$$



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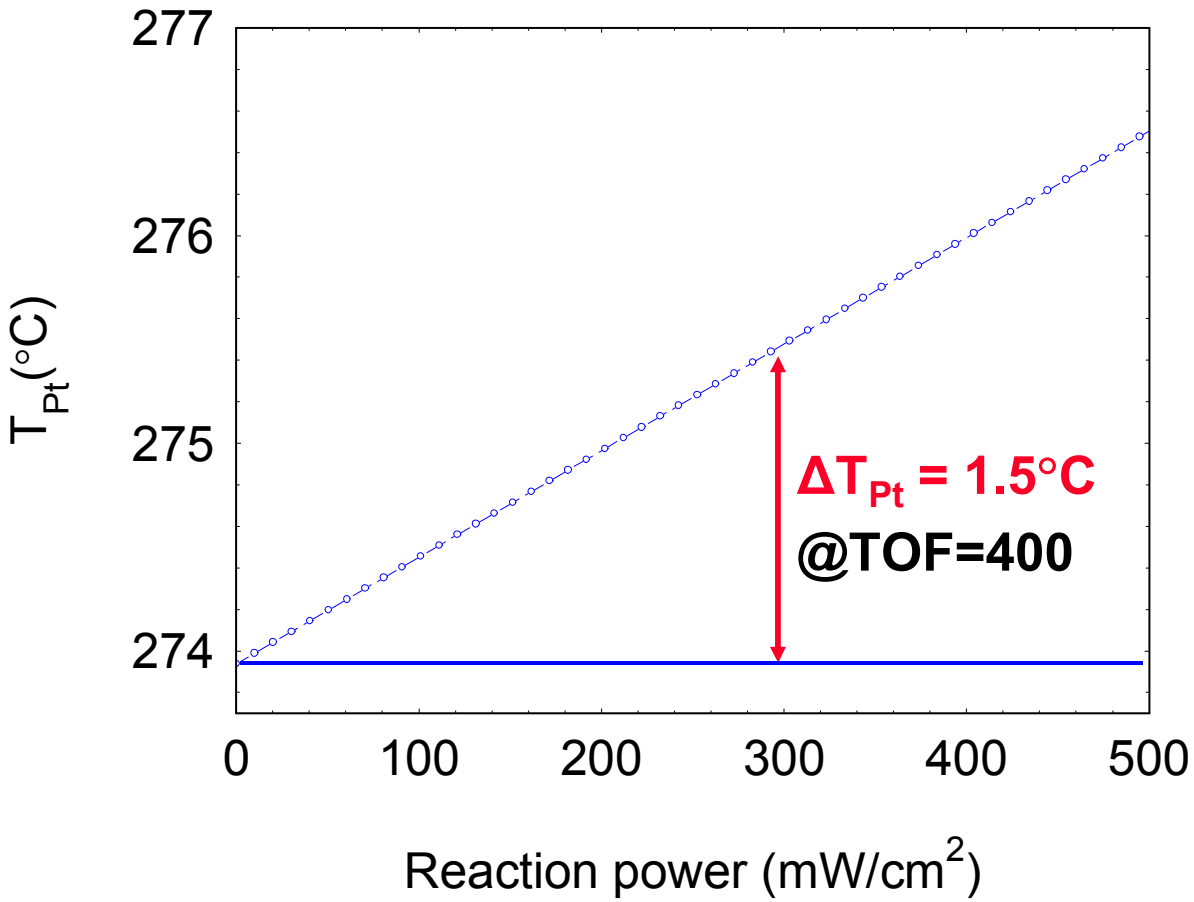
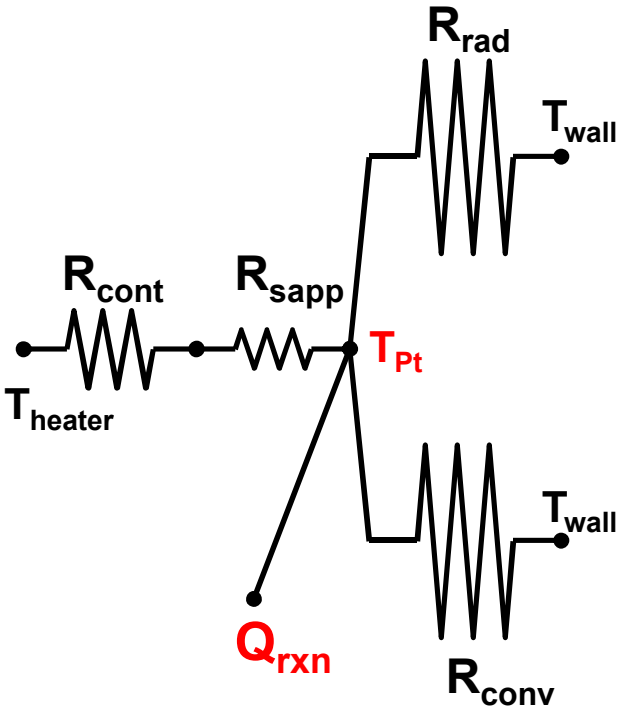
1D calculation with isothermal heater



Equivalent thermal circuit



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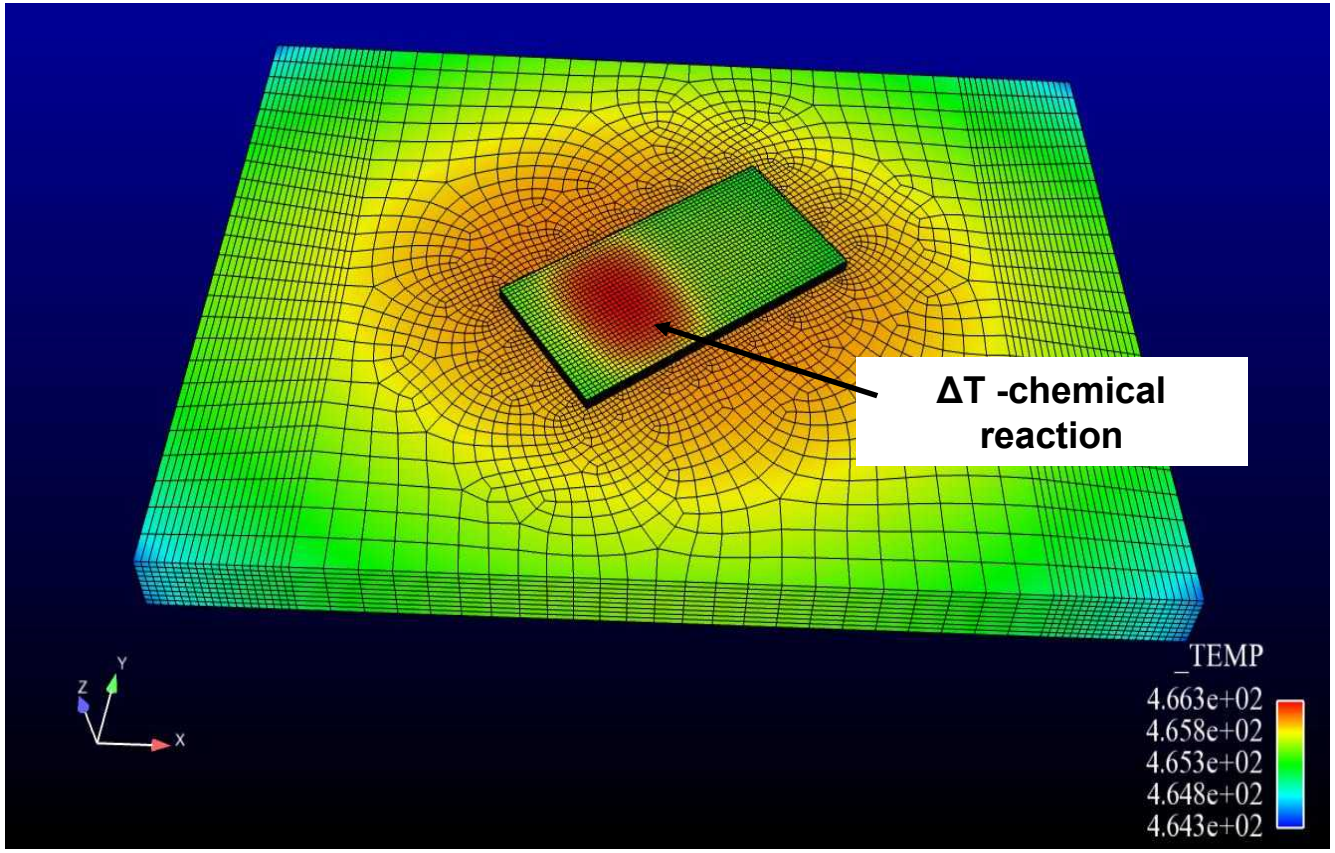
Full 3D simulation



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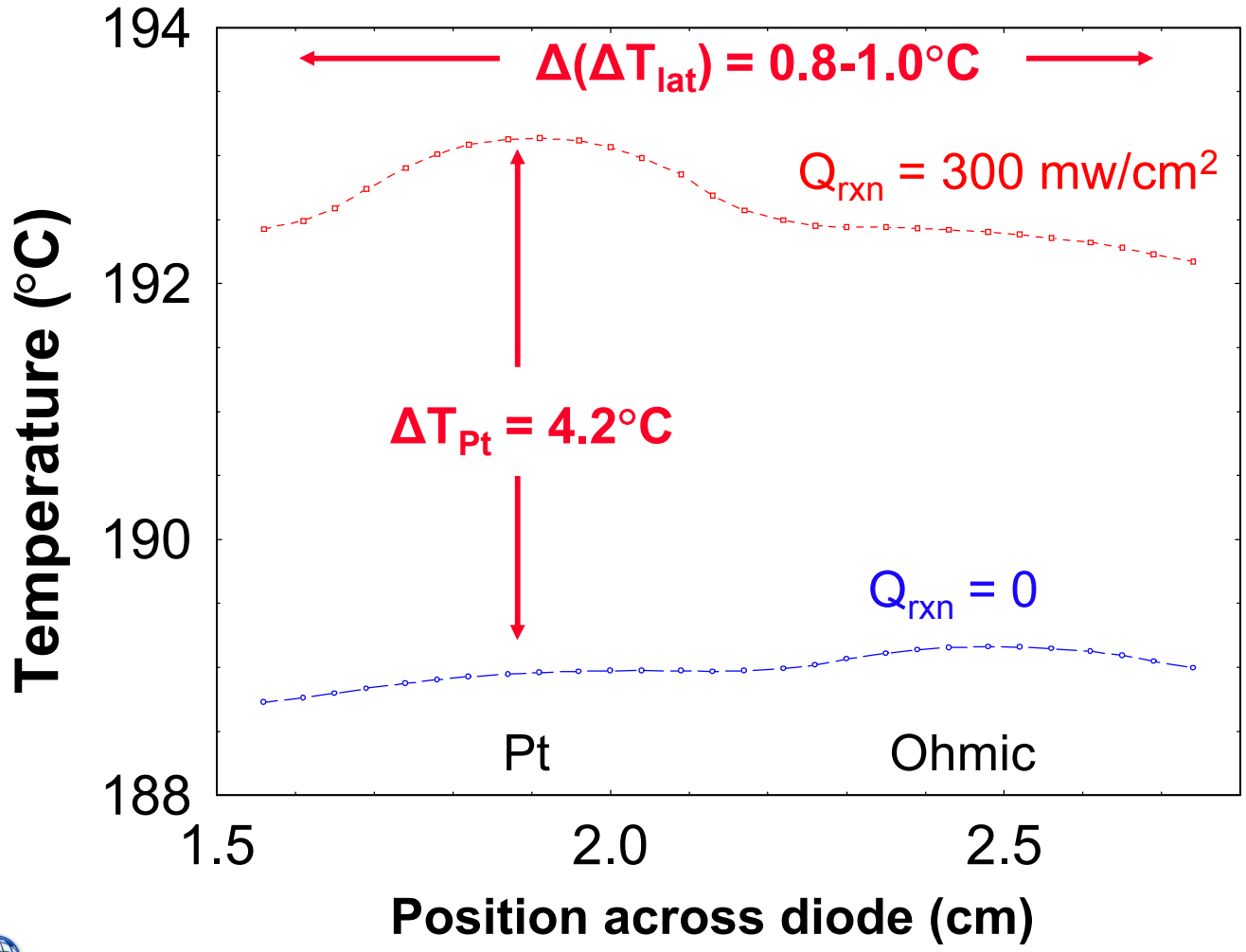
Full 3D simulation



Heater at constant power

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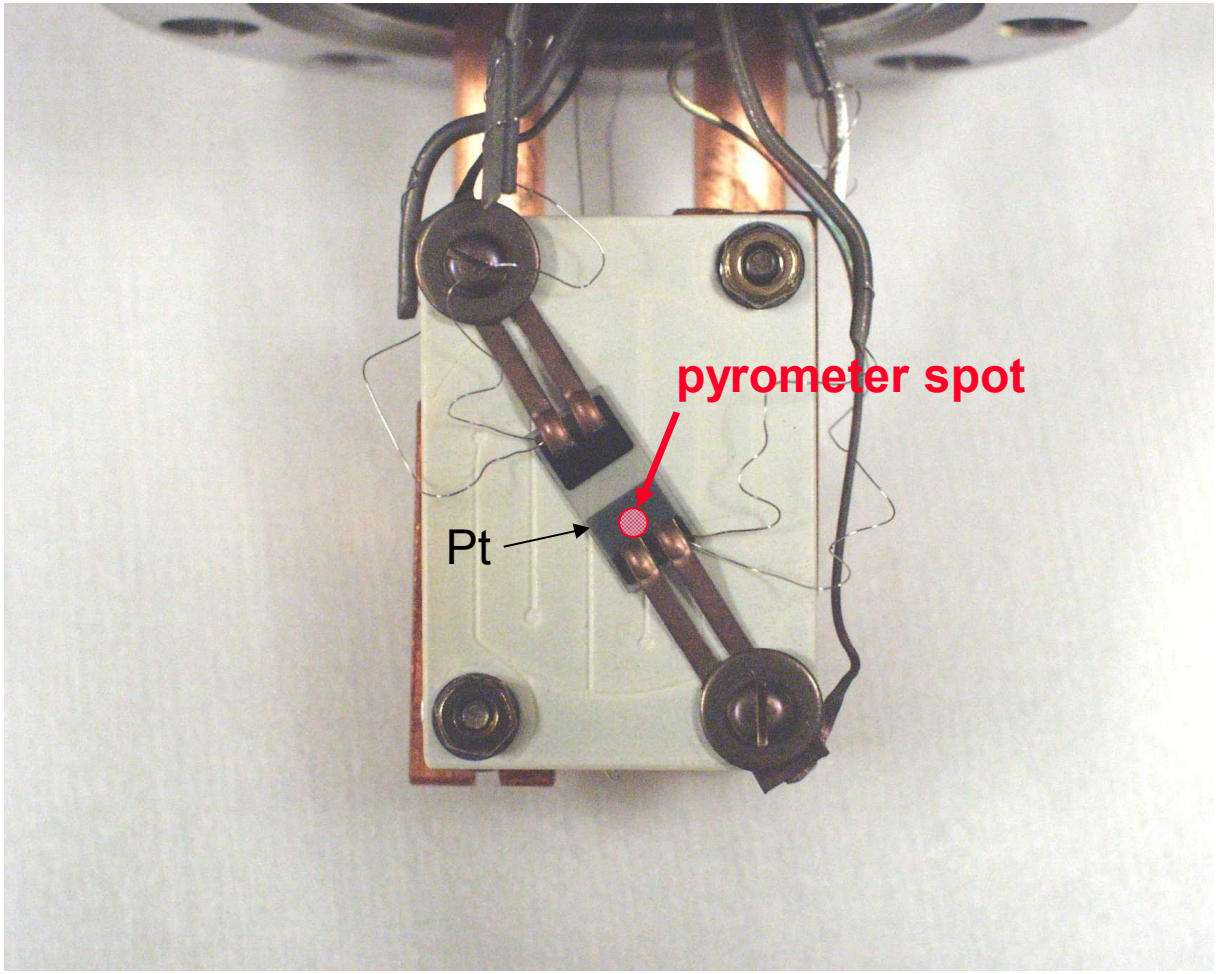
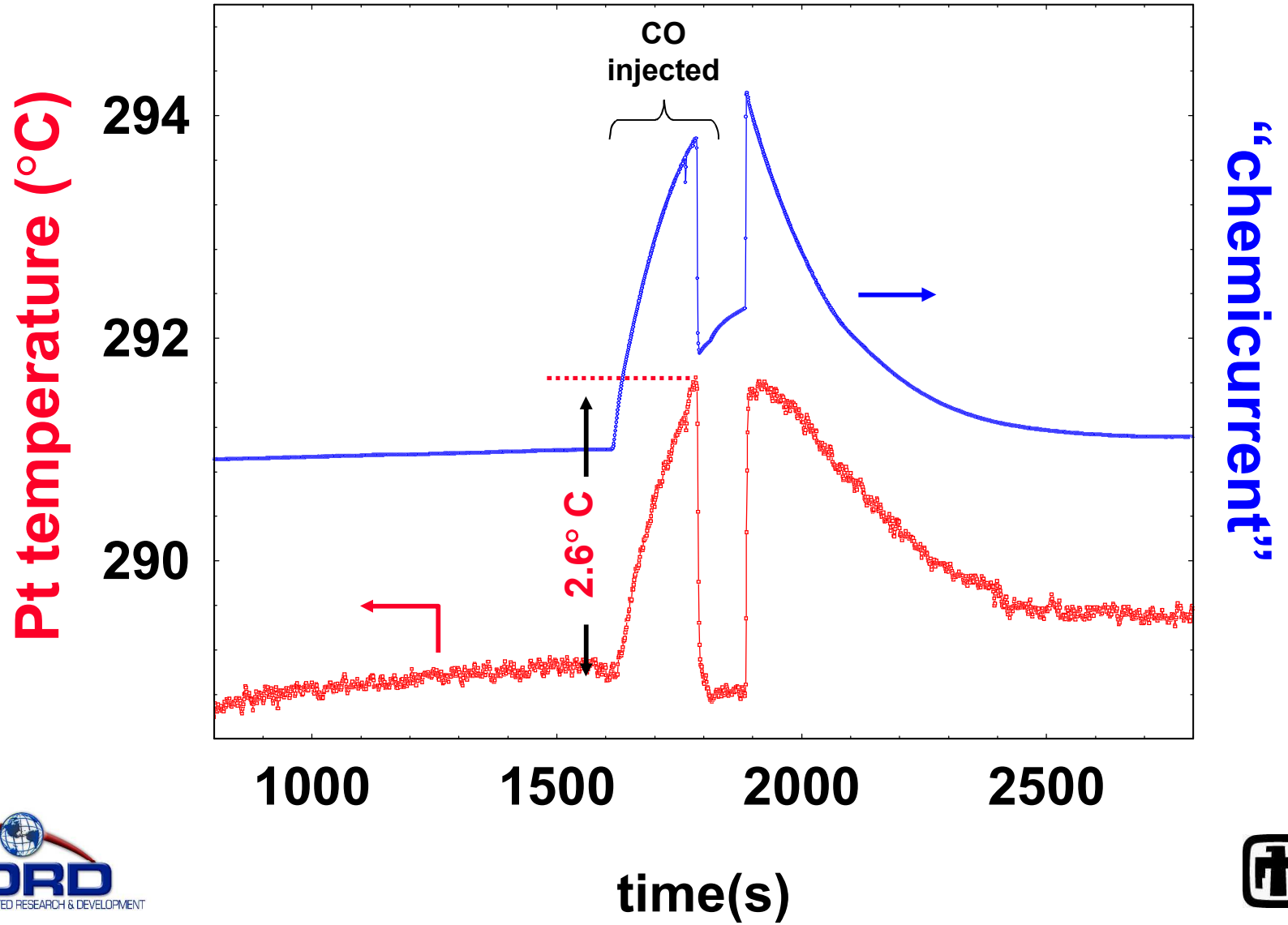
Experimental methods of temperature measurement

Nanodiode mounted with thermocouples on contacts



mid-IR (7.5 μm) pyrometer unambiguously measures Pt surface temperature rise during reaction



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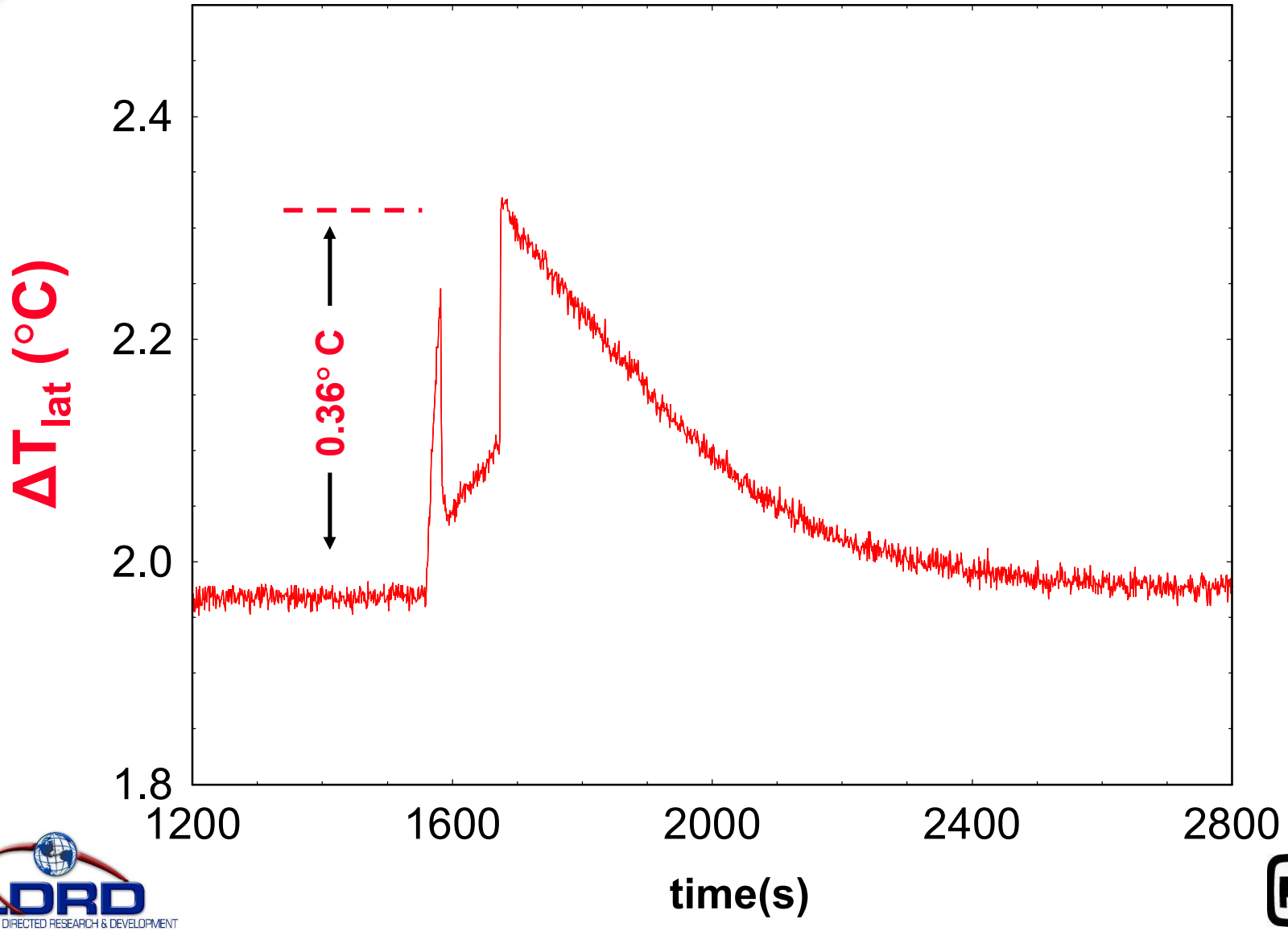
thermocouples are used to measure the lateral temperature gradient during reaction



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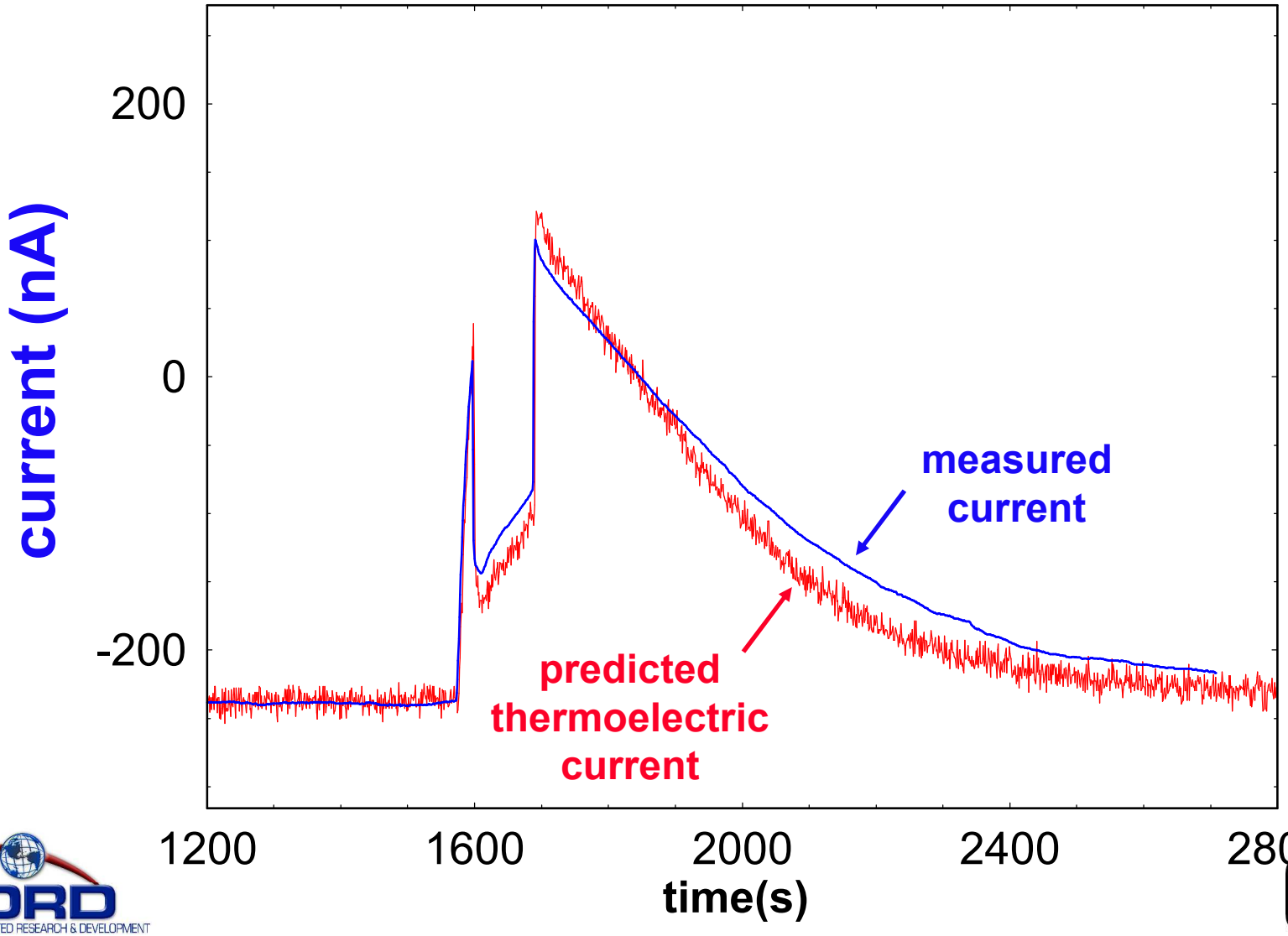
Observed current can be quantitatively explained using ΔT_{lat} , the Seebeck Coef, and the diode resistance, it is entirely due to thermoelectric voltage



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Our calculations and measurements conclusively demonstrate surface temperature rises of a 1-5 °C, and lateral temperature gradients of 0.2-1.0 °C

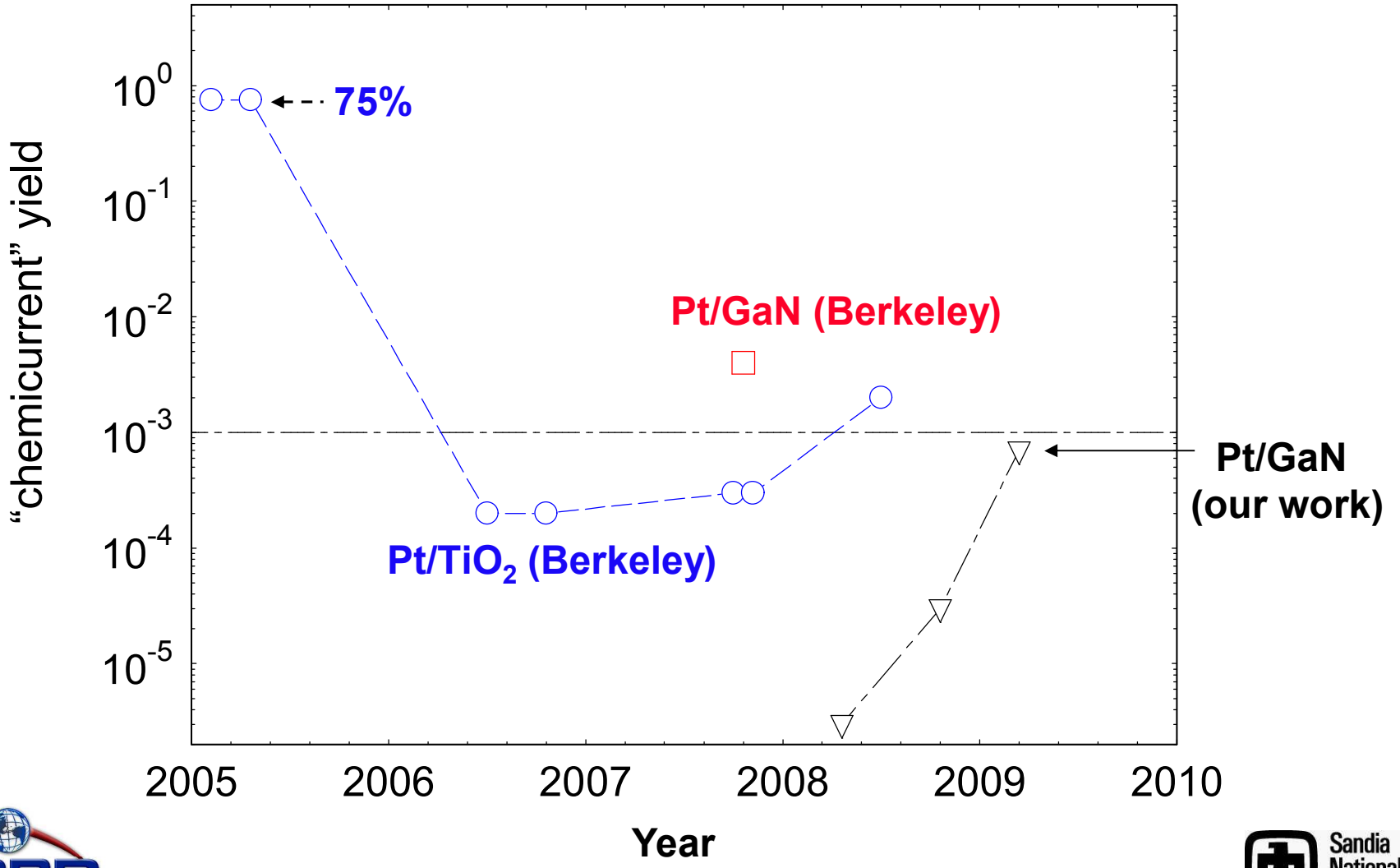
In contrast, Park et al. (Top Cat 2007) concluded that the temperature increase during reaction was negligible (< 10^{-3} °C), and therefore dismissed the thermoelectric effect

They are confusing vertical temperature gradients within the thin Pt and TiO_2 layers ($\Delta T_{\perp}$) with surface temperature changes, and lateral temperature gradients

Summary

- We have fabricated Pt/GaN and Pt/TiO_2 nanodiodes that exhibit unmistakable kinetic signatures of the CO + O_2 reaction, the electronic signal is derived from the chemical reaction
- However, the signal dependence on diode shunt resistance indicates that it is derived from a voltage source
- With appropriate temperature calculations & measurements, all attributes of the chemical signal can be qualitatively and quantitatively explained by reaction exothermicity and the thermoelectric properties of the diode
- measured current is thermoelectric in origin it is not true chemicurrent

Our yield measurements are in reasonable agreement with more recent Somorjai results (post 2005)



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Earlier work regarding ballistic (hot) electrons and surface chemical reactions

1999-2007: Several papers by Nienhaus (U. Duisburg-Essen) and McFarland (UCSB) reported *transient* hot electron formation (chemicurrents) by reactions of a variety of chemical species on an assortment of Schottky diodes.

Gases	Diodes
O_2, NO, NO_2, H_2O C_2H_4, C_2H_6, C_6H_6, CO_2, Xe, H, O,	Au/Ge, Pd/SiO_2, Cu/Si, Ag/Si, Fe/Si

- Generation efficiency correlated with binding energy, but always ≤ 1%

2005: Four papers by Somorjai (Berkeley) on "Catalytic nanodiodes", used the steady-state CO oxidation reaction to achieve up to ~75% quantum yield (electrons/CO_2)

We became interested for possible micropower applications; results could be extrapolated to power conversion efficiencies of 20-30%

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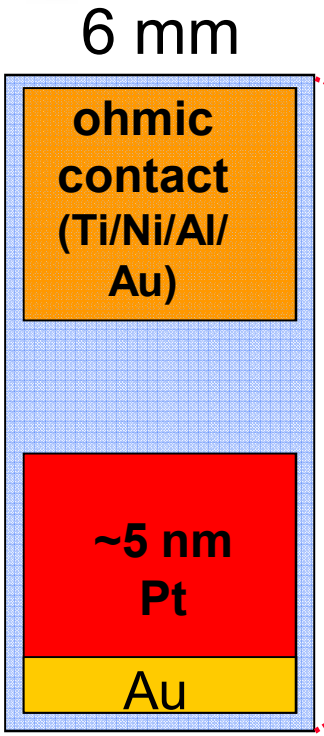
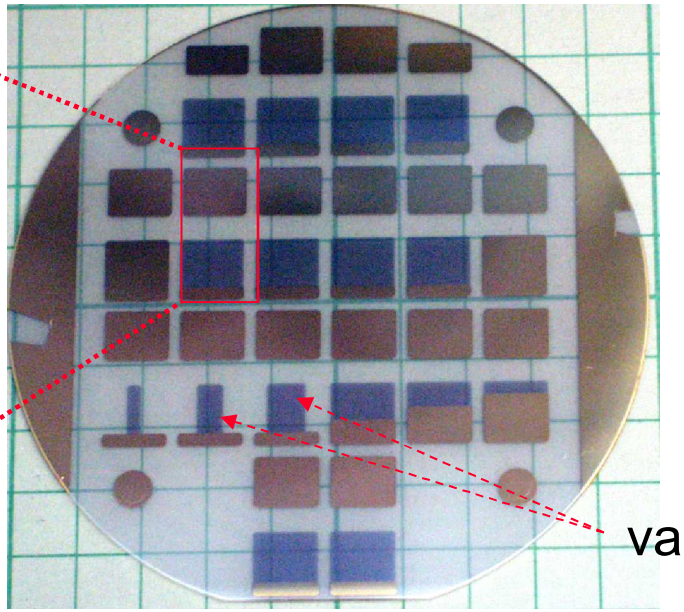
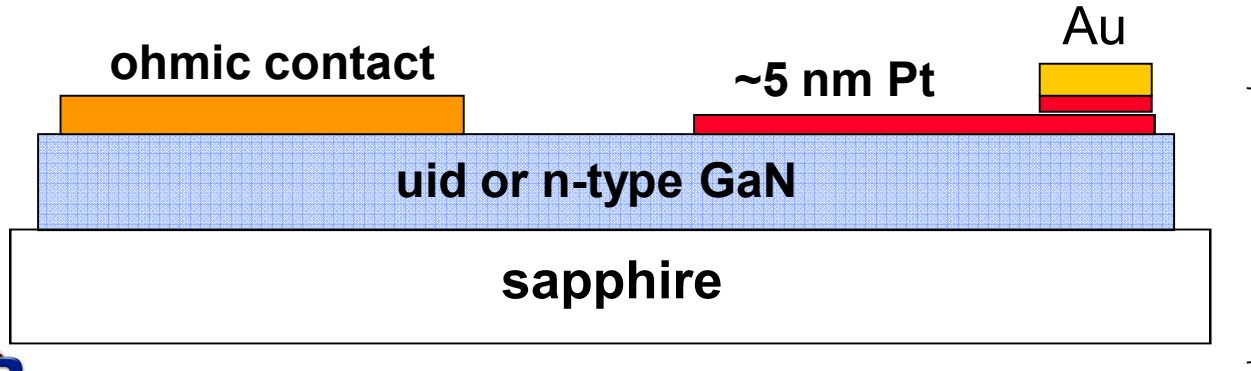
Schottky diode structure



2” wafer before dicing



variable Pt area
4-20 mm^2



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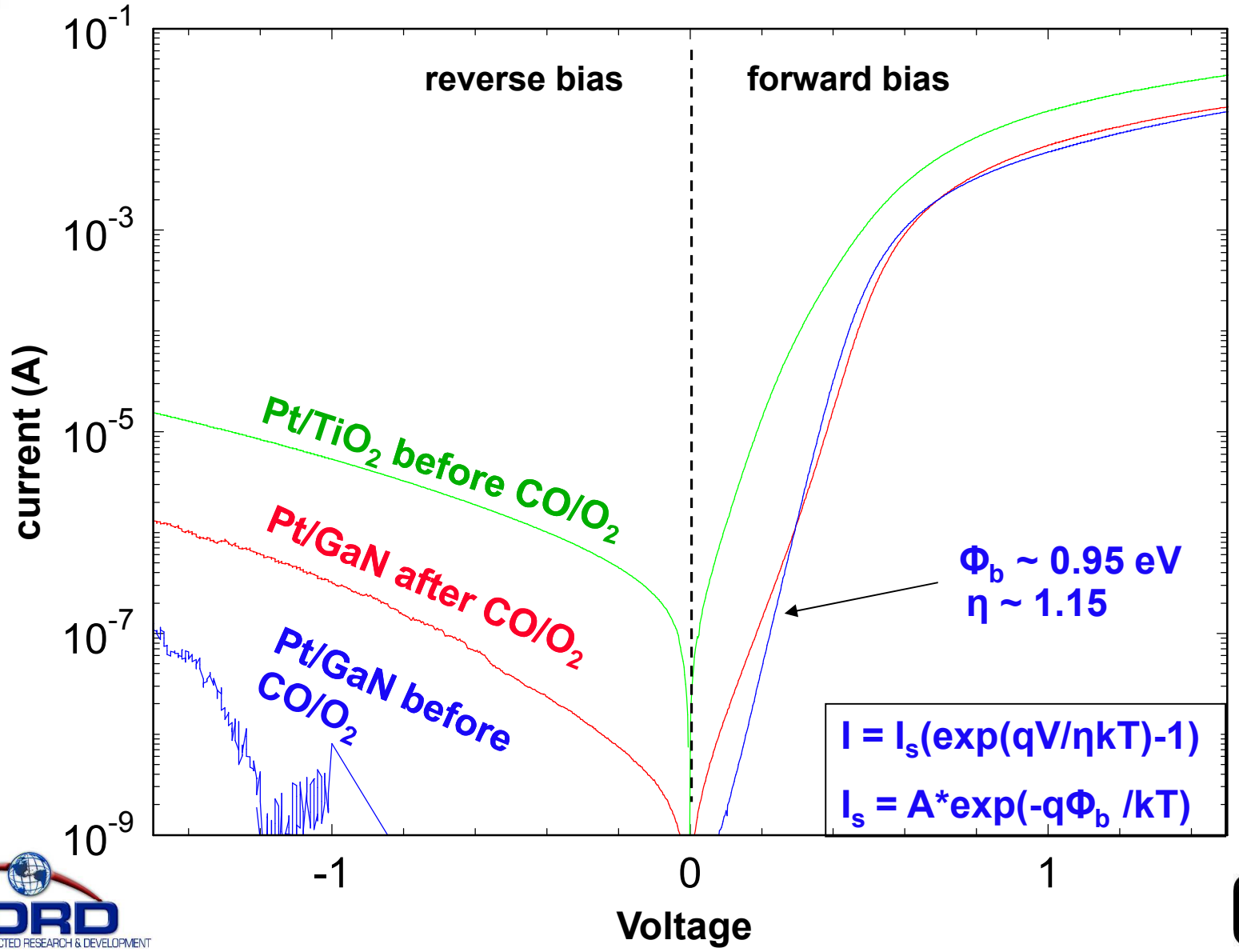
I-V curves for Pt/GaN(uid) and Pt/TiO_2 diodes



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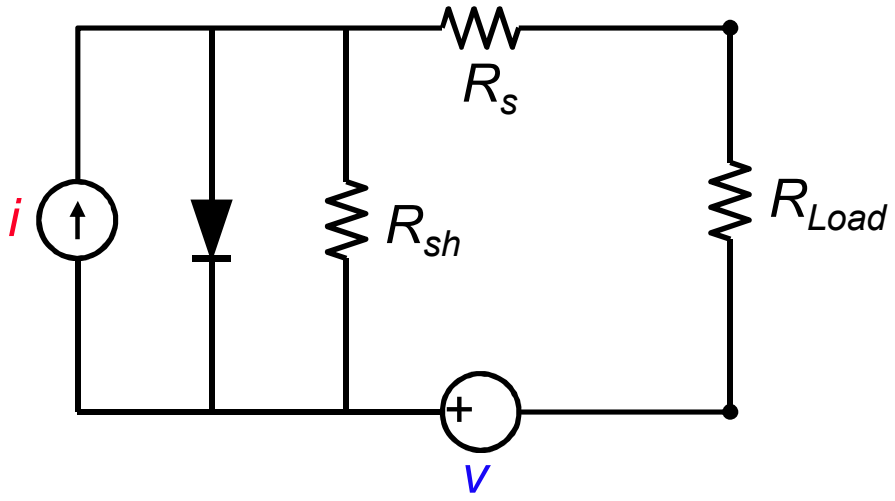
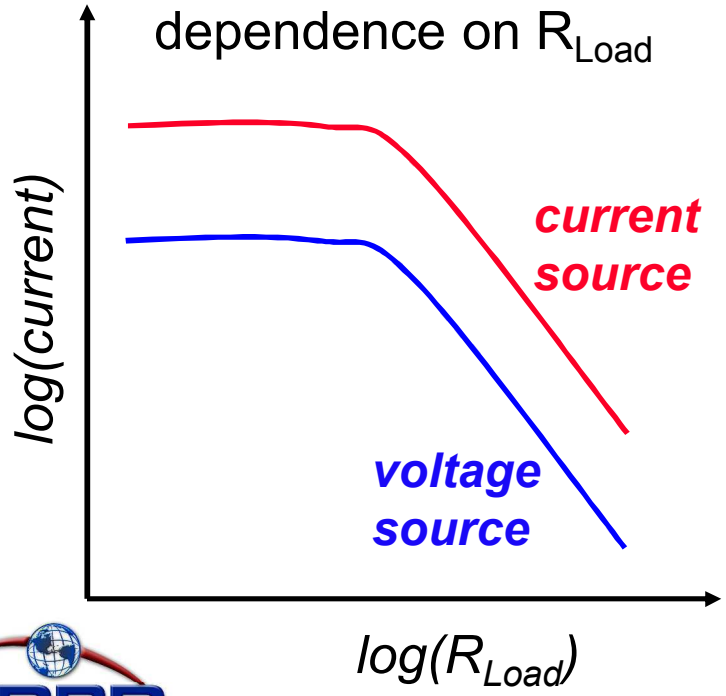
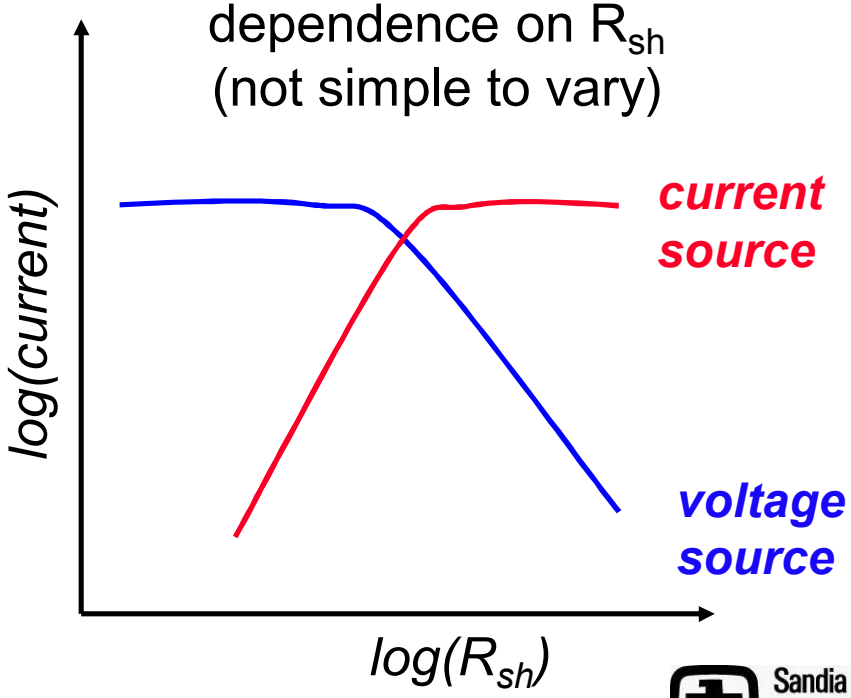
How can you differentiate a current source from a voltage source when shunt (R_{sh}) and series (R_s) resistance are present?



Both show same dependence on R_{Load}



But different dependence on R_{sh} (not simple to vary)



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Other indications we have simply made a sensitive thermal detector

- Response depends on Schottky diode temperature (T) and the lateral temperature difference (ΔT_{lat})

Signal from V_{TE} has 2 terms (may be of opposite sign)

Seebeck coef

temperature dependence of diode impedance

$$dI(\Delta T, T) = \frac{\partial V_{TE}}{R \partial \Delta T} d\Delta T - I \frac{\partial R}{R \partial T} dT$$

this term is responsible for most of the chemical signal under normal conditions

we can amplify this term with external bias voltage

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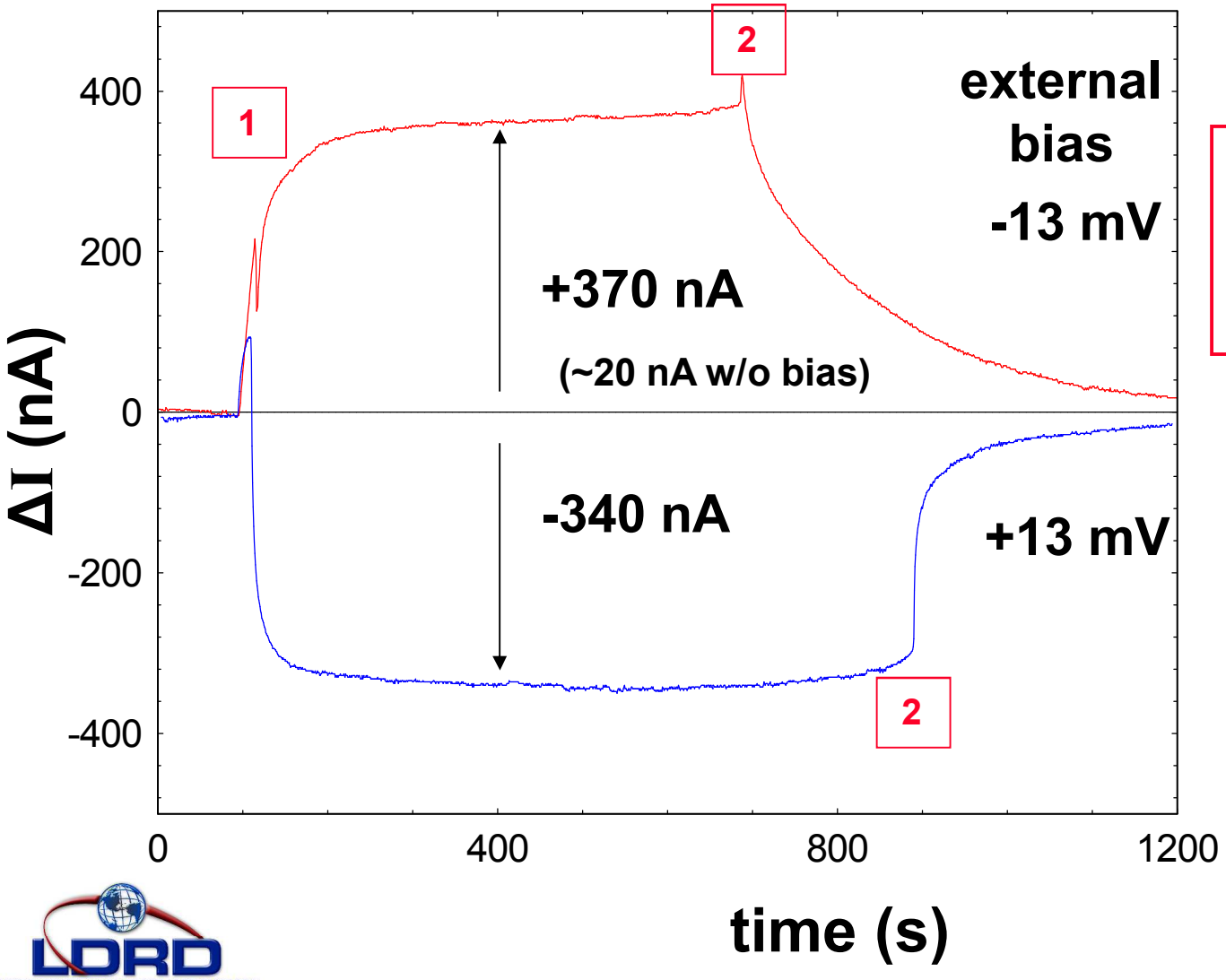
Thermal signal amplification by small external bias voltage



Most of the chemical signal changes polarity as bias voltage is reversed

signal indicates a temperature rise of ~ 15°C

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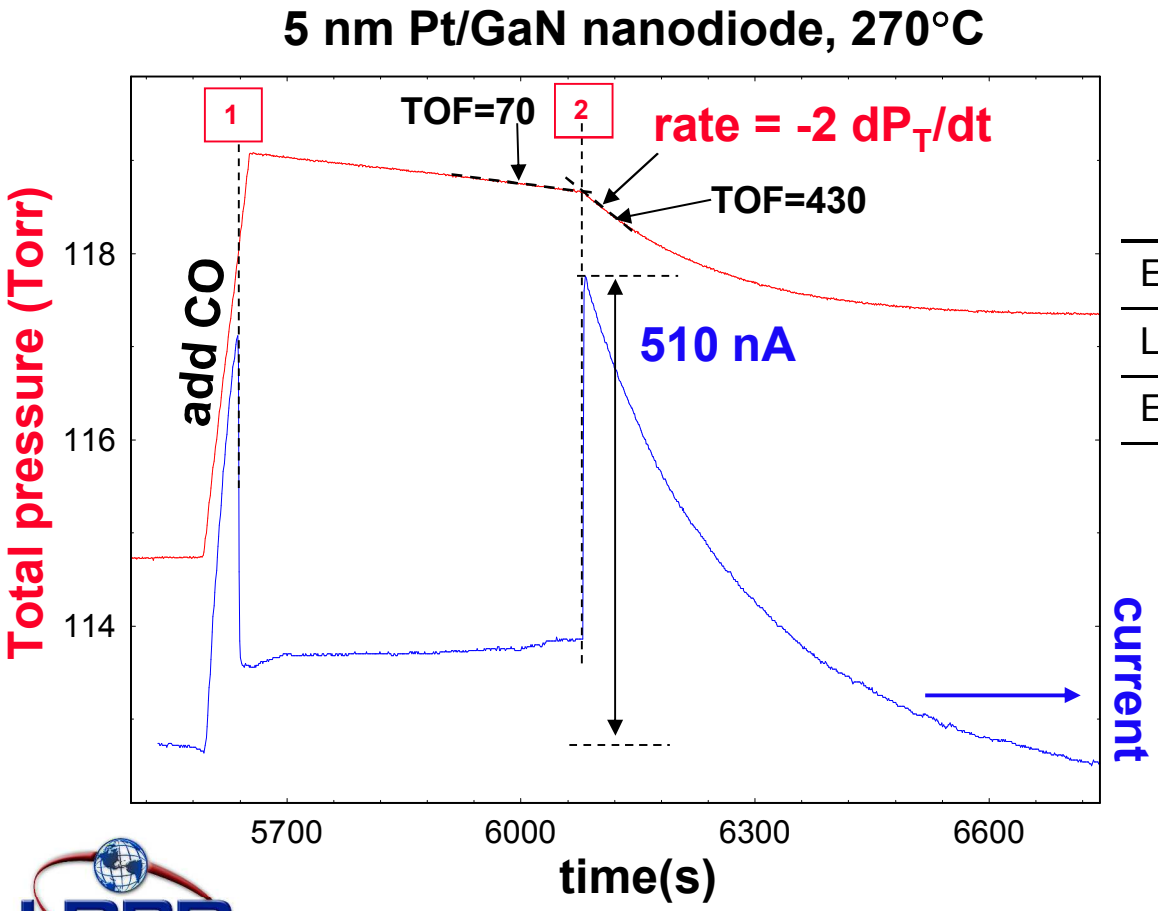
In order to measure the electron generation yield of the process we also measure the production rate of CO_2

Use a pressure drop method to measure reaction rates;

$CO + ½ O_2 \rightarrow CO_2$ (net loss of ½ mole)



Sandia results	Highest I_{sc}	Yield Electrons/CO_2
Early 2006	**200 nA**	**1-3e-6**
Late 2008	**700 nA**	**3e-5**
Early 2009	**2000 nA**	**7e-4**

"Improvements" are due to increasing GaN doping levels

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Review of Somorjai's results

2005 At least 4 papers and several popular press articles; Initial results for Pt/TiO_2 , **ε** as high as 0.75!, currents as high as 40 μA (area ~1 mm^2) at only 80°C. Reported strong dependence on metal thickness. Pt/GaN devices were less efficient, but had currents of >200 nA/mm^2 at 150 °C

2006 3 papers, some repetition but results are generally less impressive than 2005 papers in terms of currents and temperatures. Some discussion of "thermoelectric" current. Efficiency not discussed

2007 October JPhysChem. **ε** = 2e-4 to 4e-3, now GaN better than TiO_2. Temp range higher than earlier work, currents mostly in 50-500 nA. More discussion of "thermoelectric current

2008 July, Nanolett. **ε** = .001-.003, $Pt/Au/TiO_2$. Currents 50-150 nA. Some discussion of Seebeck coef.

2008 Aug, ACS Meeting, when asked (by Creighton) why they could not reproduce the 75% result (2005), Somorjai replied that it was a device "fabrication" problem.