The Search for True Chemicurrent from Catalytic Nanodiodes

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GaN deposition – Dan Koleske

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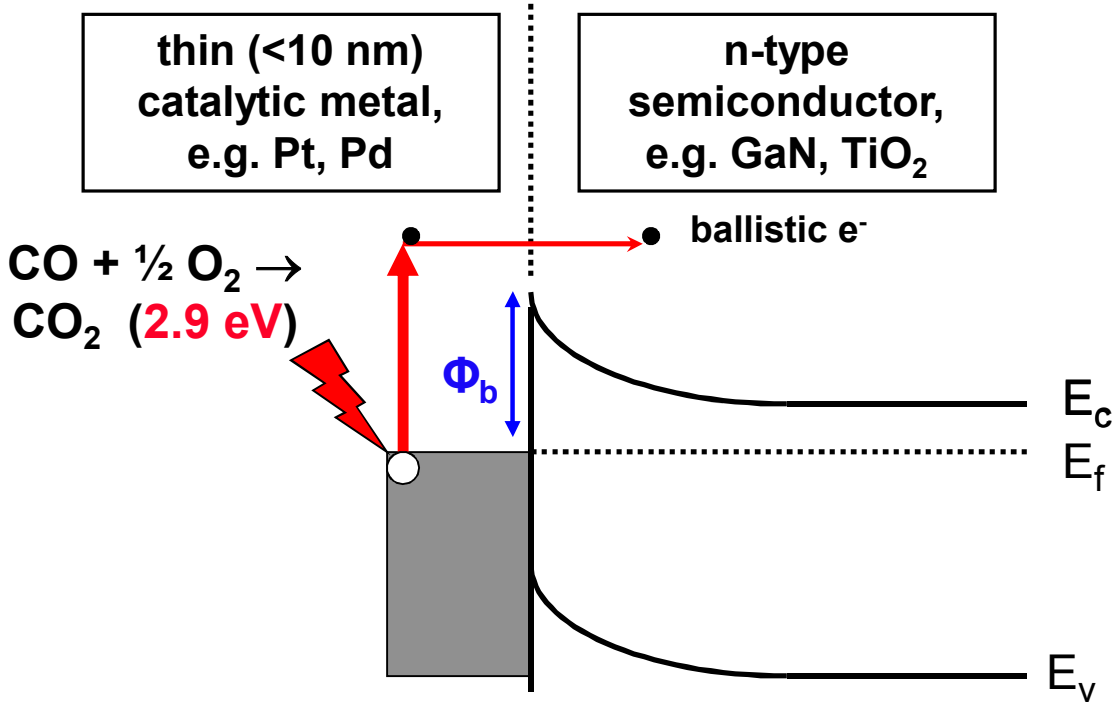
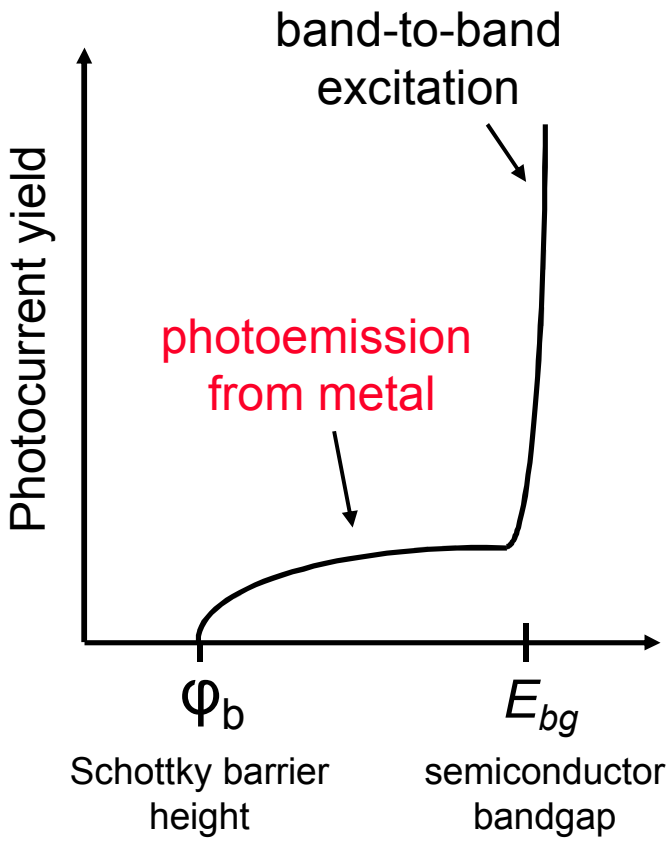
What is a "Catalytic Nanodiode"?

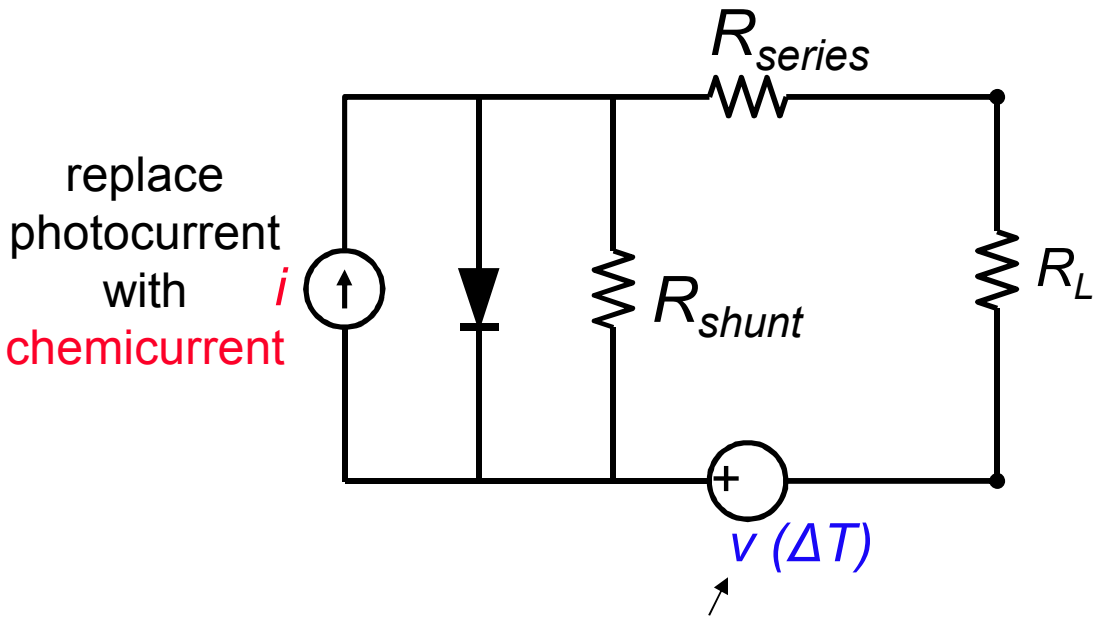
- **The catalytic nanodiode is a simple Schottky diode that converts chemical energy directly into electrical energy, via electronic excitation, i.e. hot electrons**
- **Somorjai et al. reported (2005) a reaction quantum yield (electrons/CO_2) up to ~75% for the CO oxidation reaction on Pt/TiO_2, coined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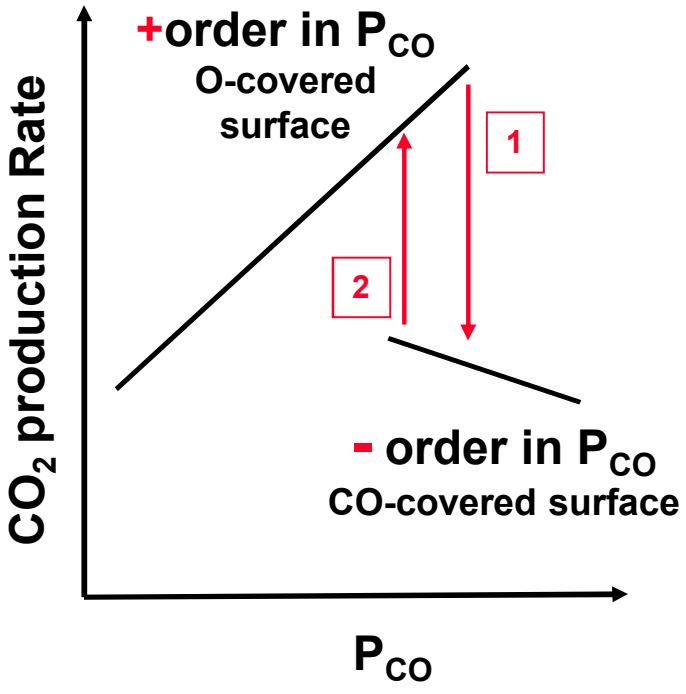
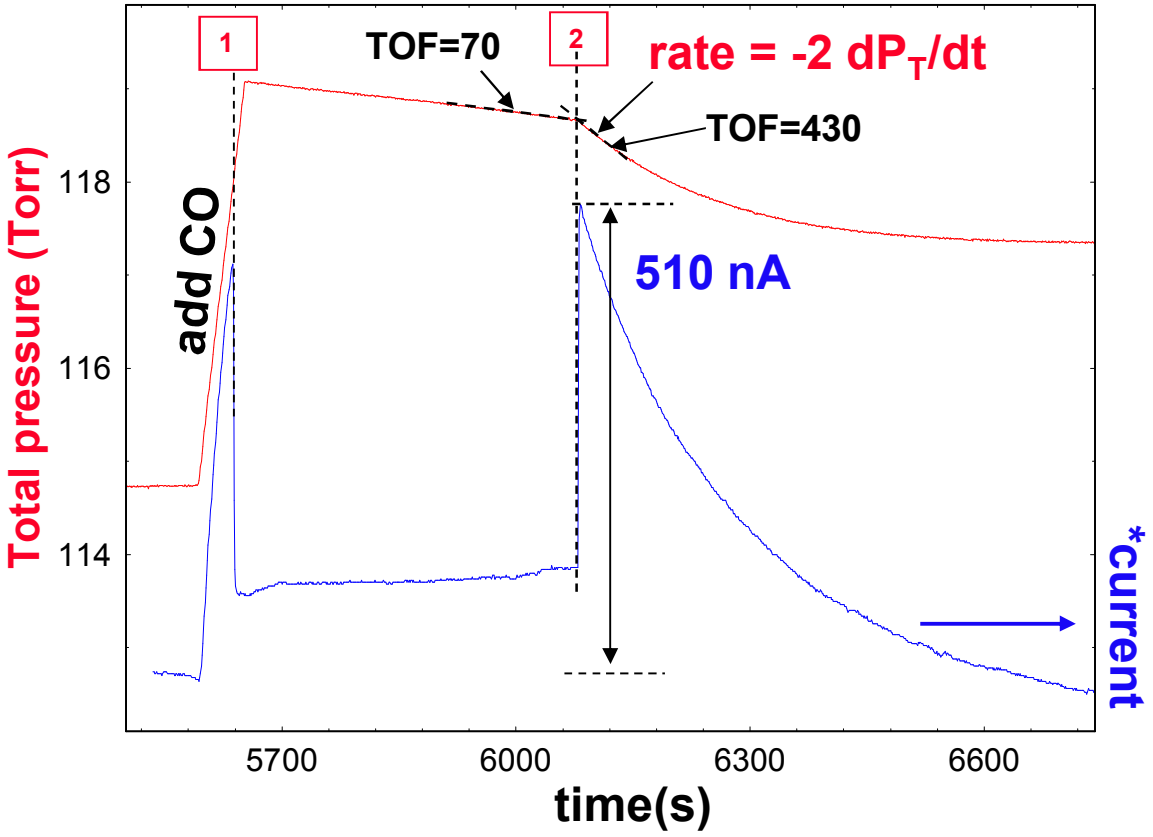
Kinetic phase transition during CO oxidation on Pt is observable using the nanodiode current



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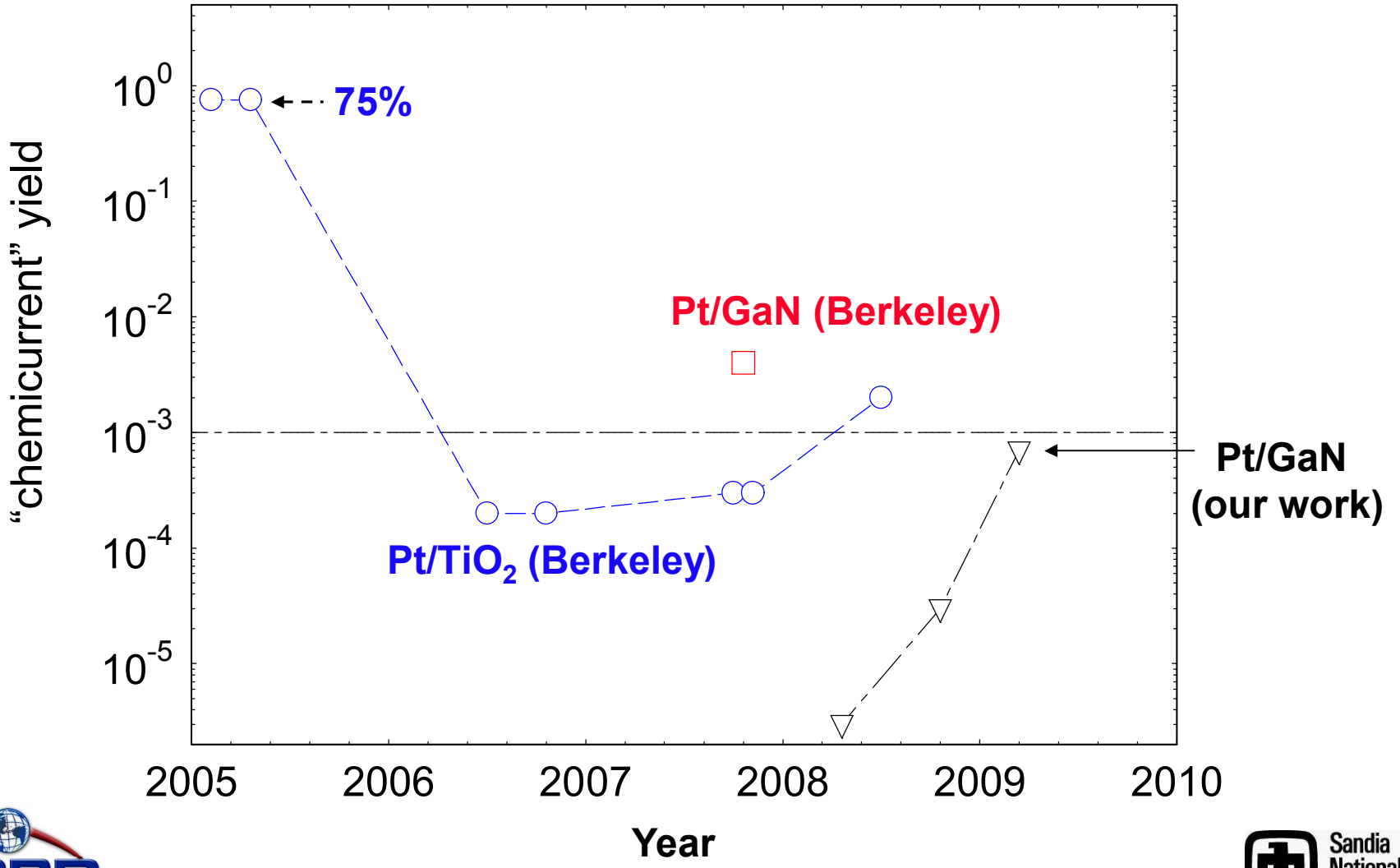
Our yield measurements are in reasonable agreement with more recent Somorjai results (post 2005)



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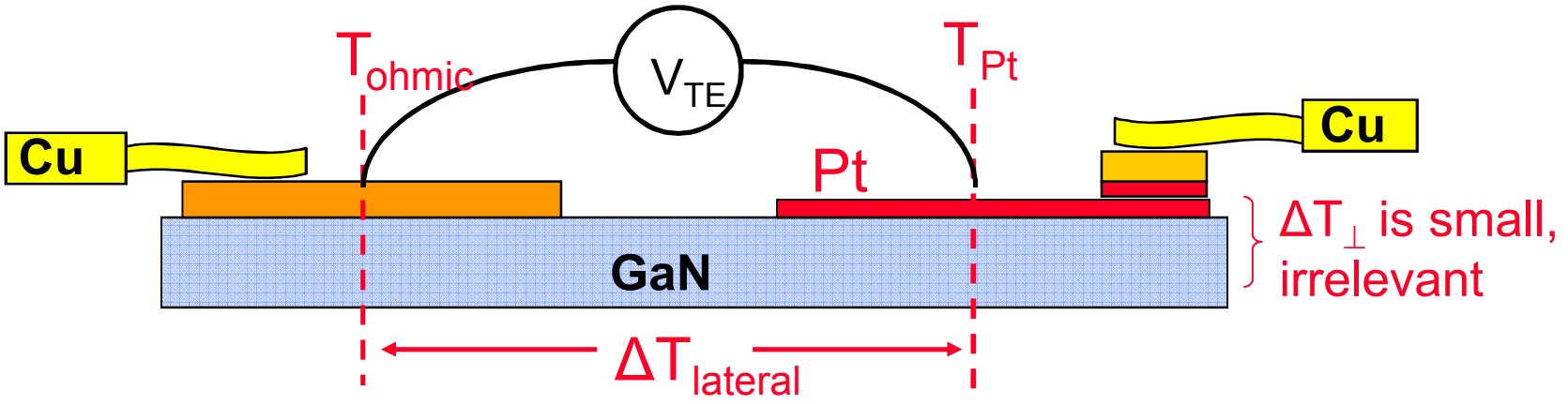
Is the electronic signal due to "chemicurrent" or is it derived from a voltage source?



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

V_{TE} is mostly determined by:

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

2) the <u>lateral temperature difference</u>, ΔT_{lat}

only need ΔT_{lat} ~1°C

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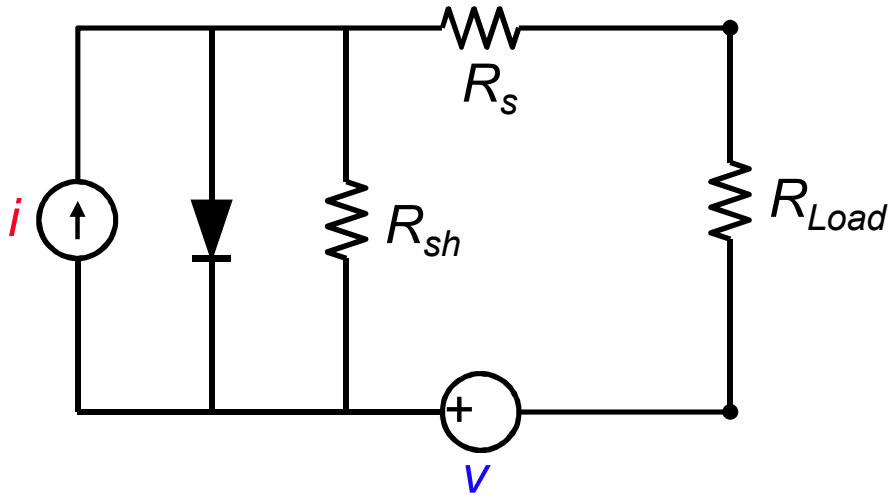
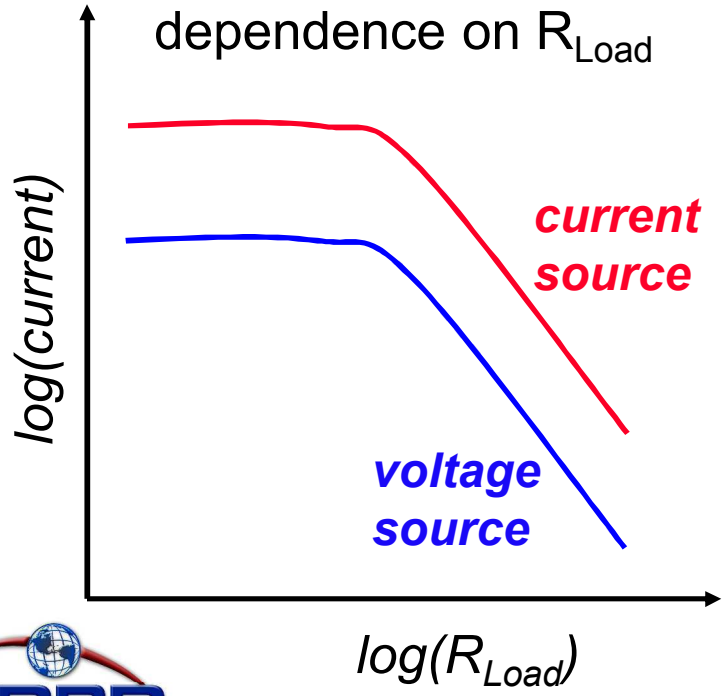
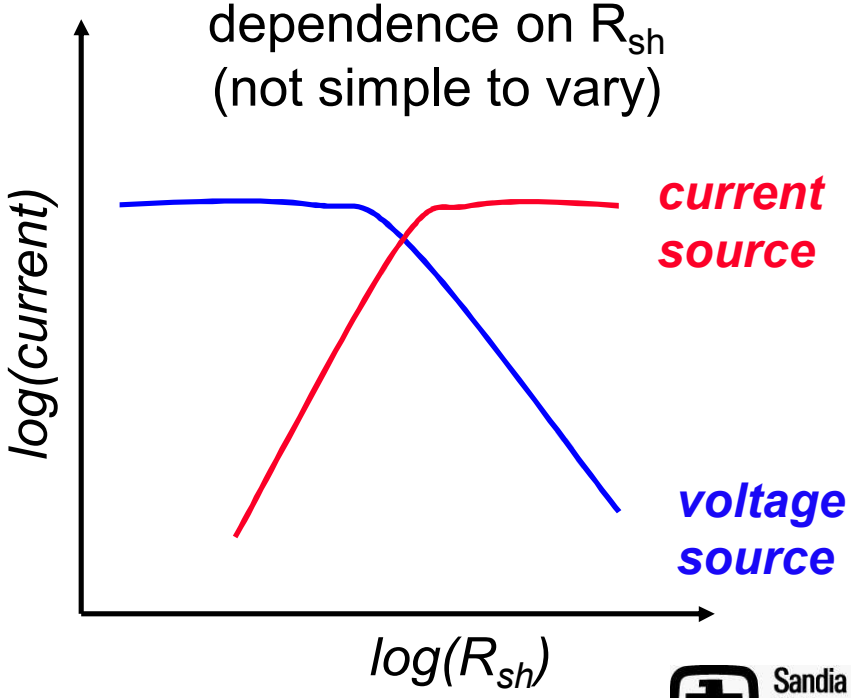
How can you differentiate a current source from a voltage source when shunt (R_{sh}) and series (R_s) resistance are present?



Both show same dependence on R_{Load}



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



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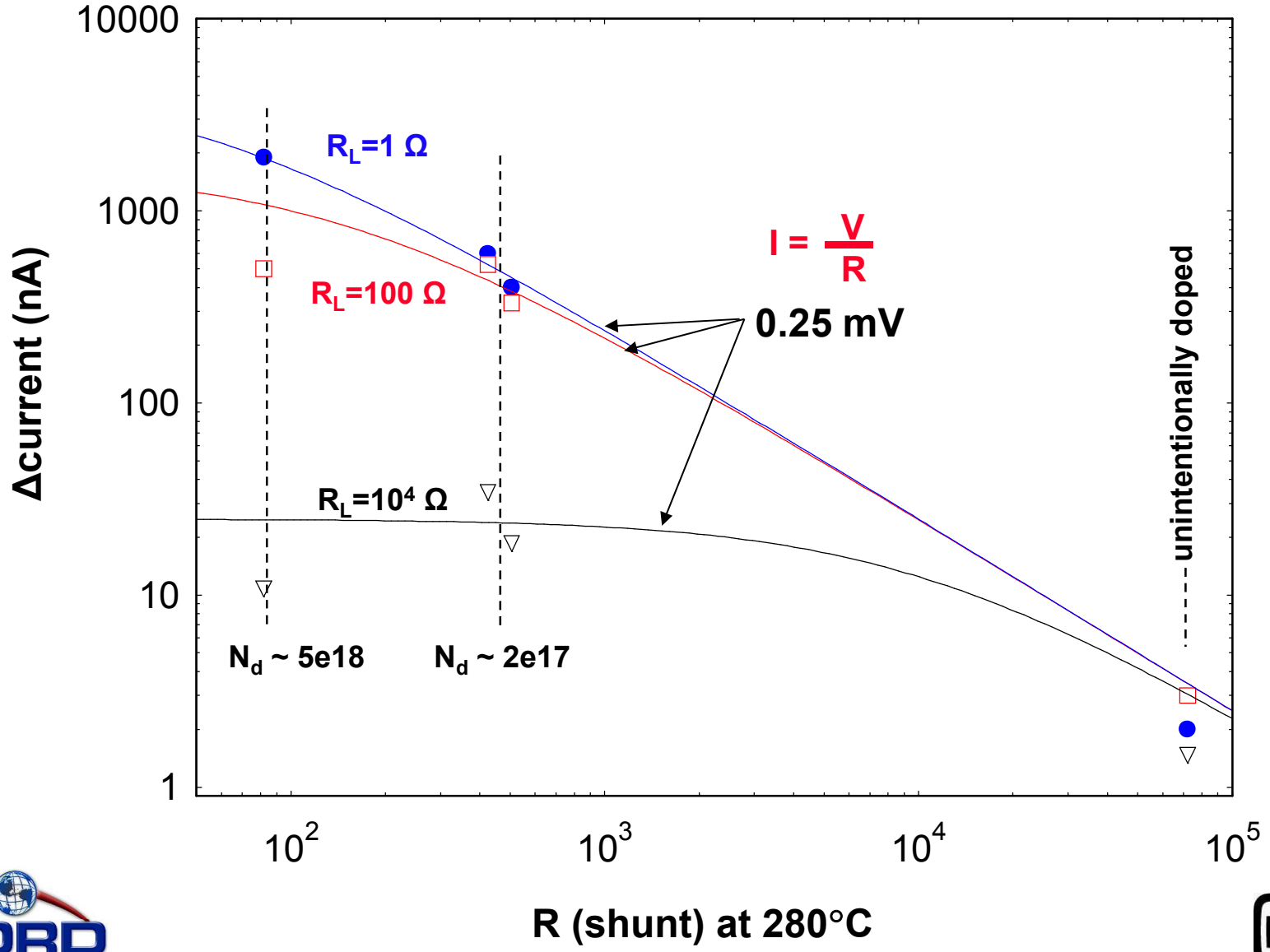
Vary R_{shunt} by varying GaN doping level, behavior is indicative of a voltage source



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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:

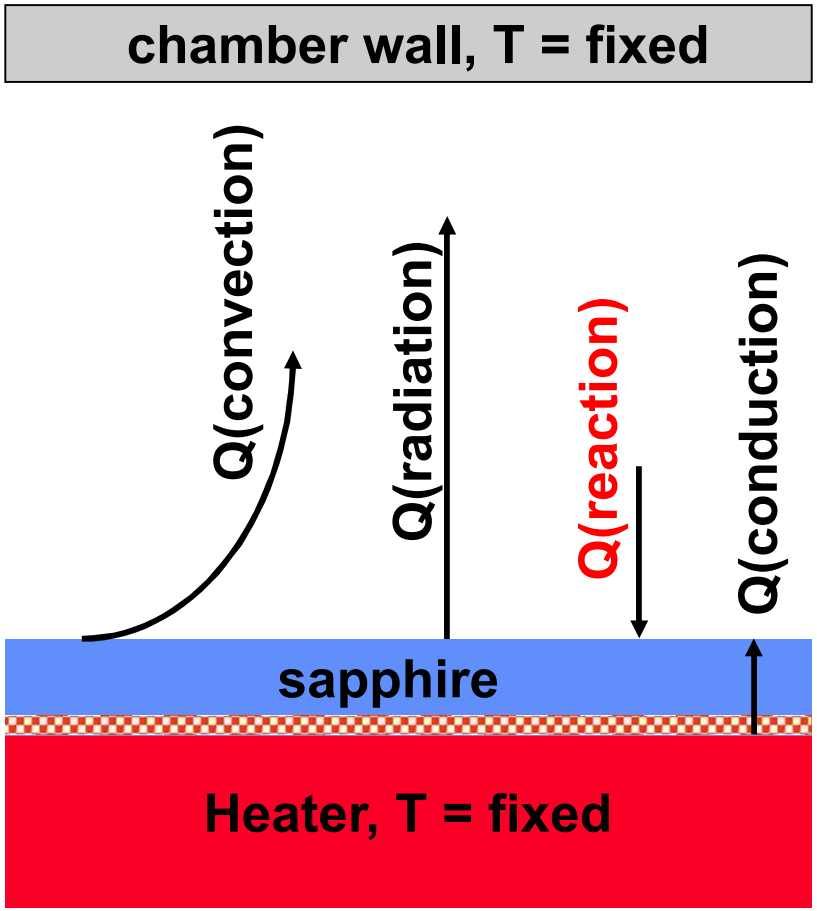
- "Simple" 1D and quasi-2D calculations
- Full 3D simulations of entire reactor

Experimental:

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

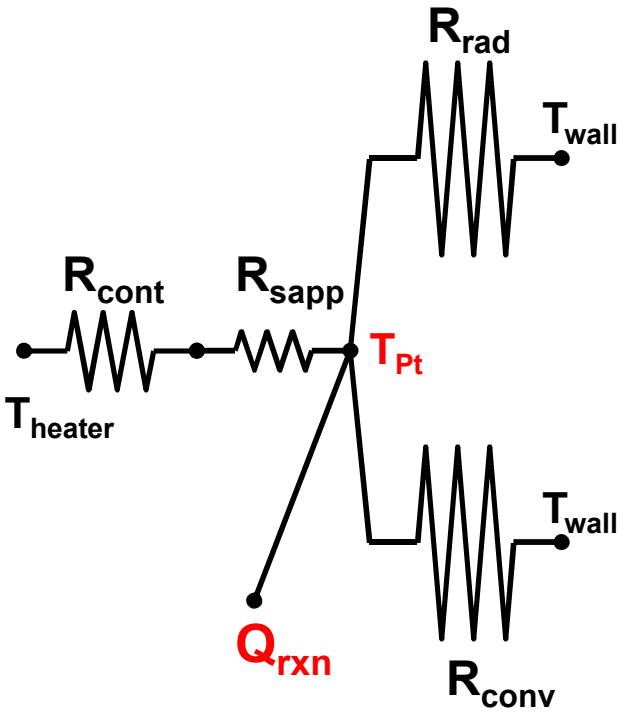
1D calculation with isothermal heater

Physical model



Equivalent thermal circuit

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



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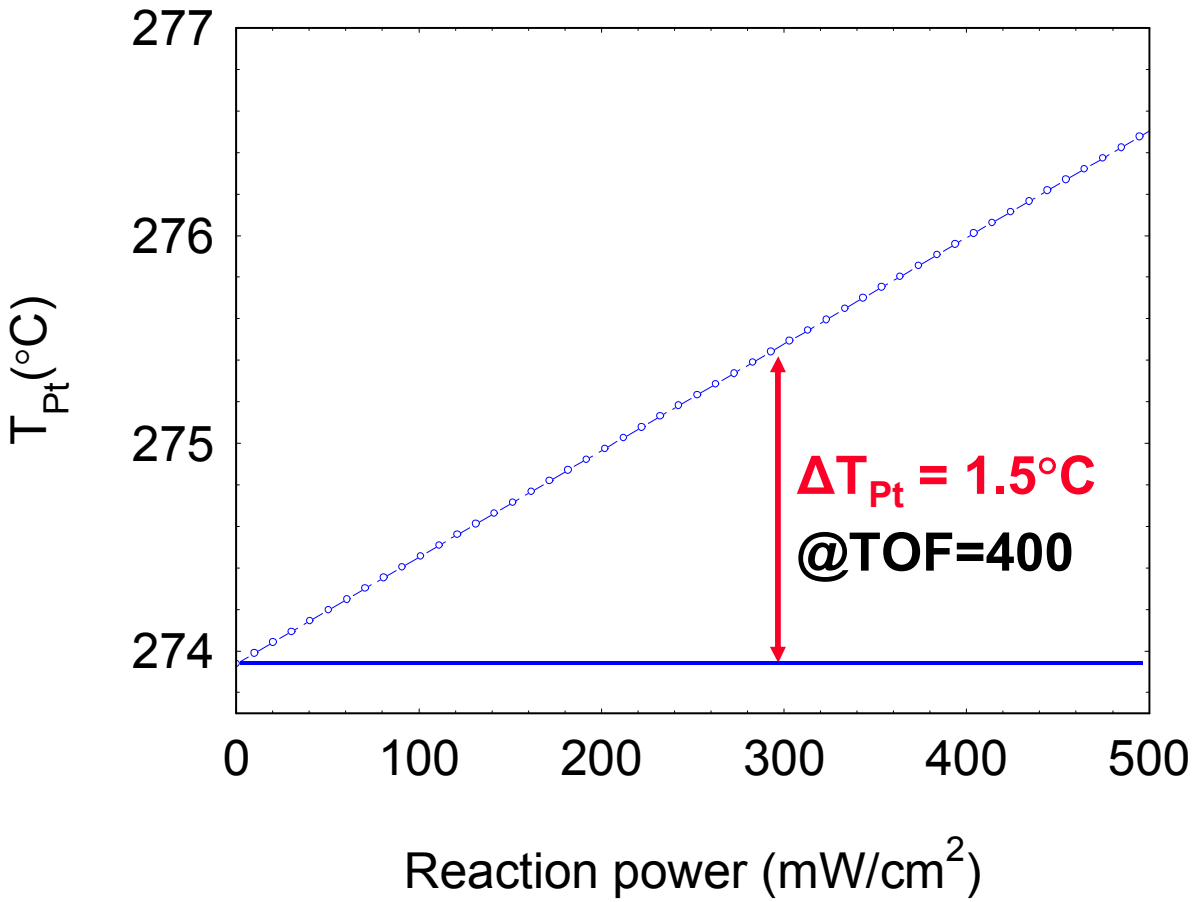
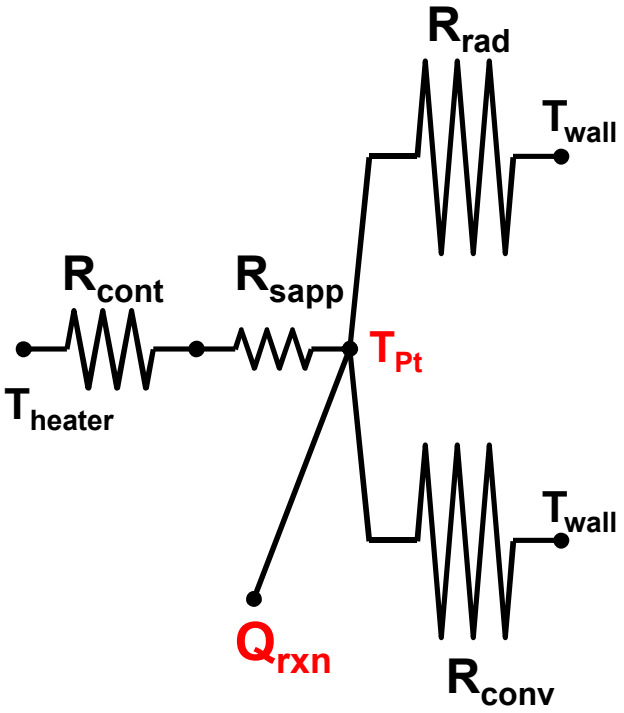
1D calculation with isothermal heater



Equivalent thermal circuit



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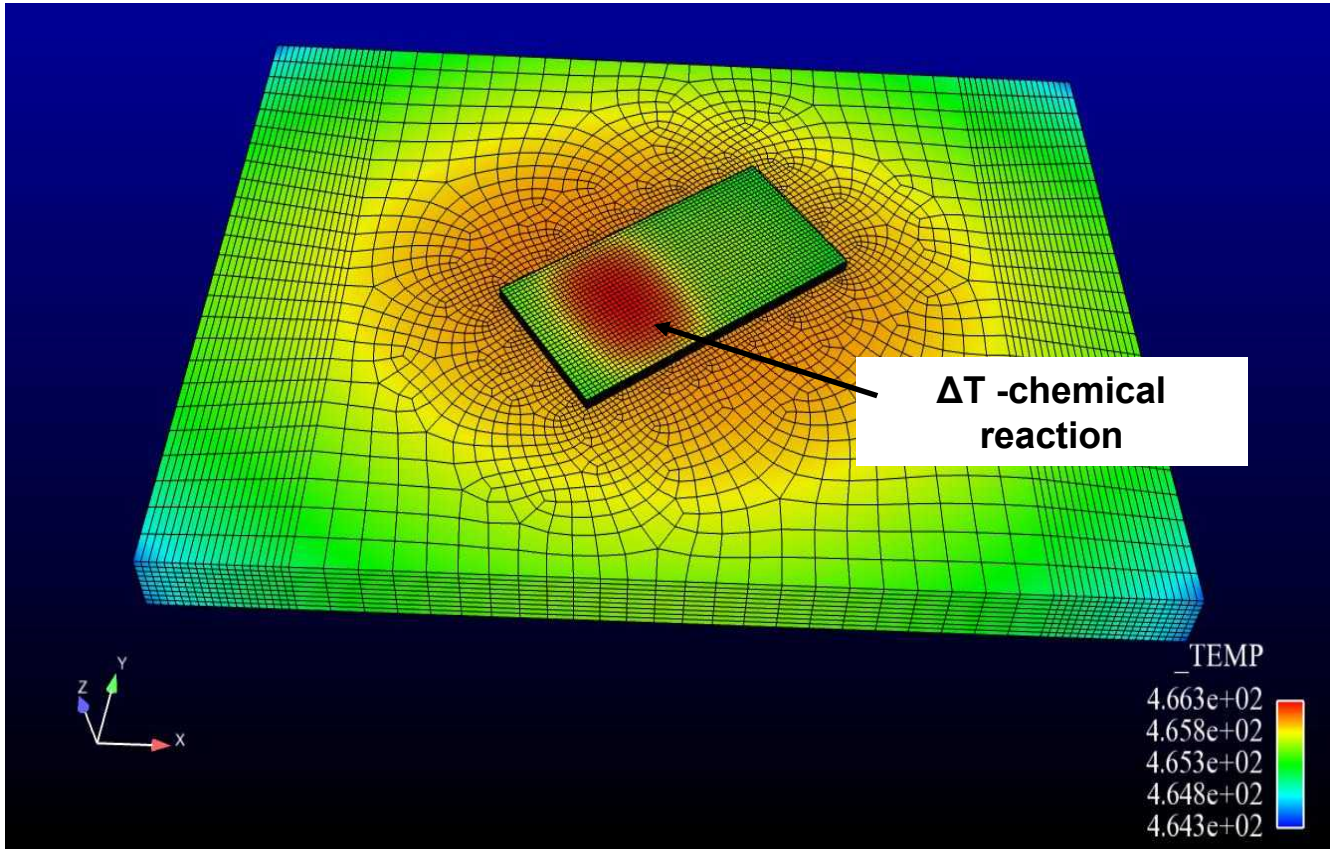
Full 3D simulation



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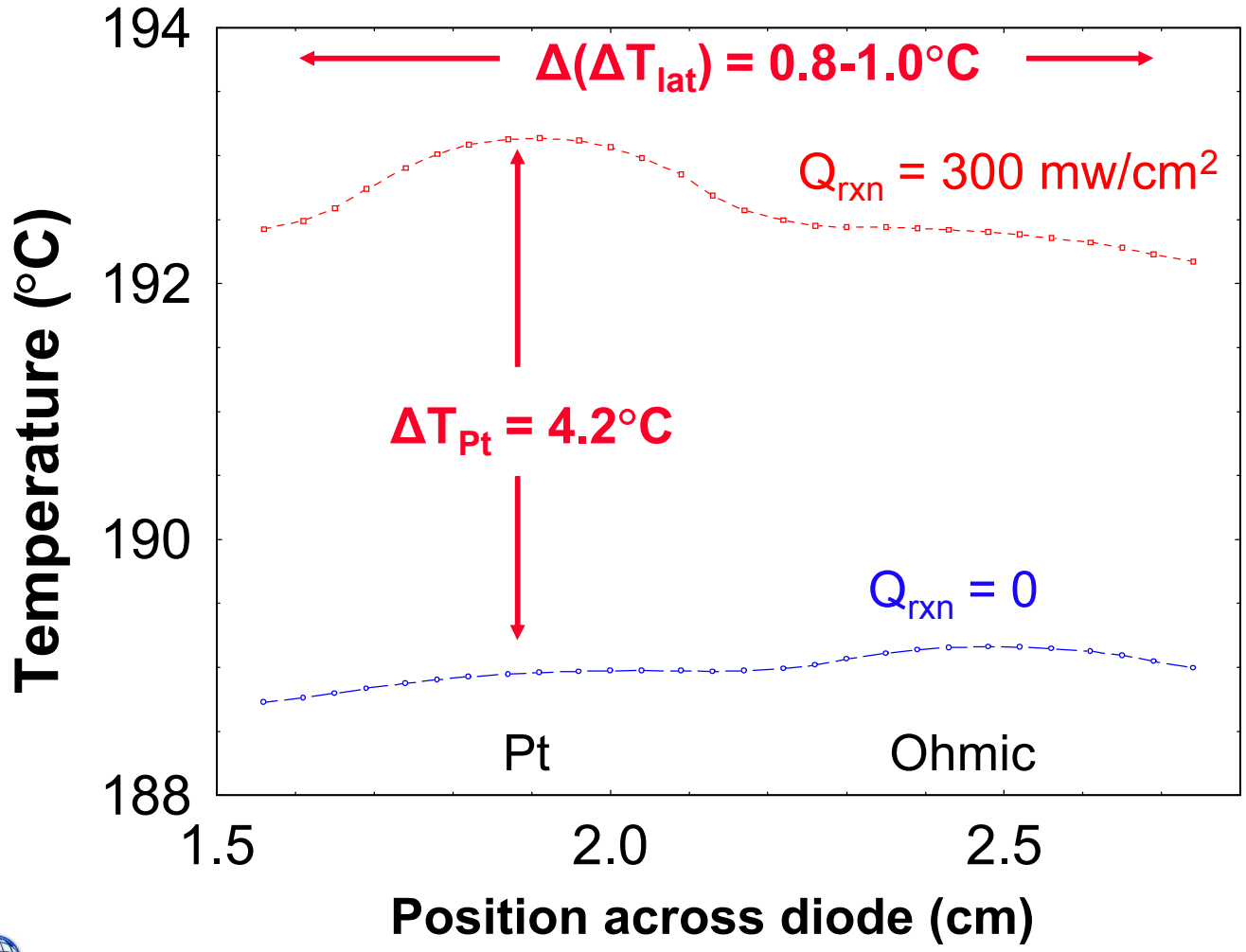

Heater at constant power

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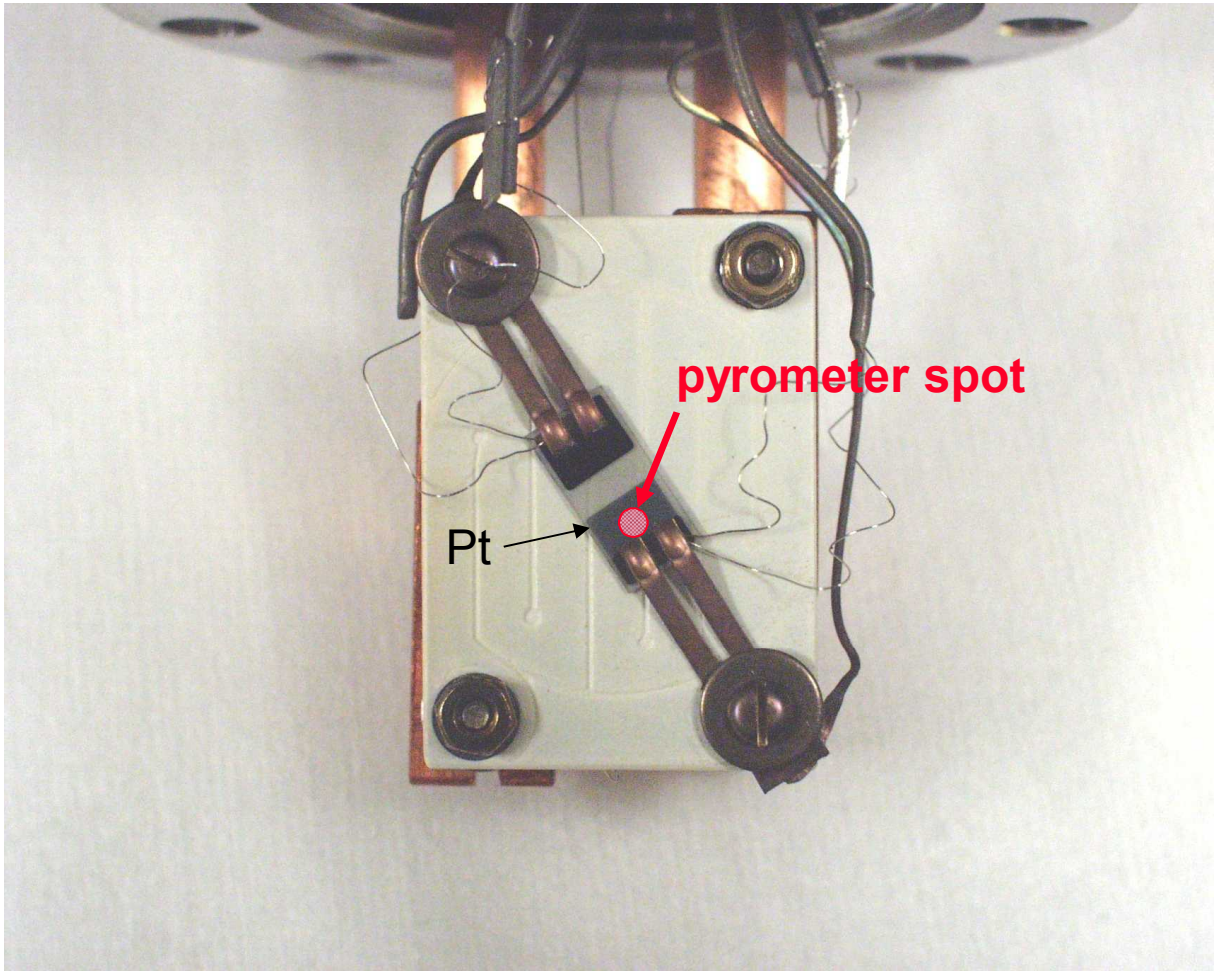
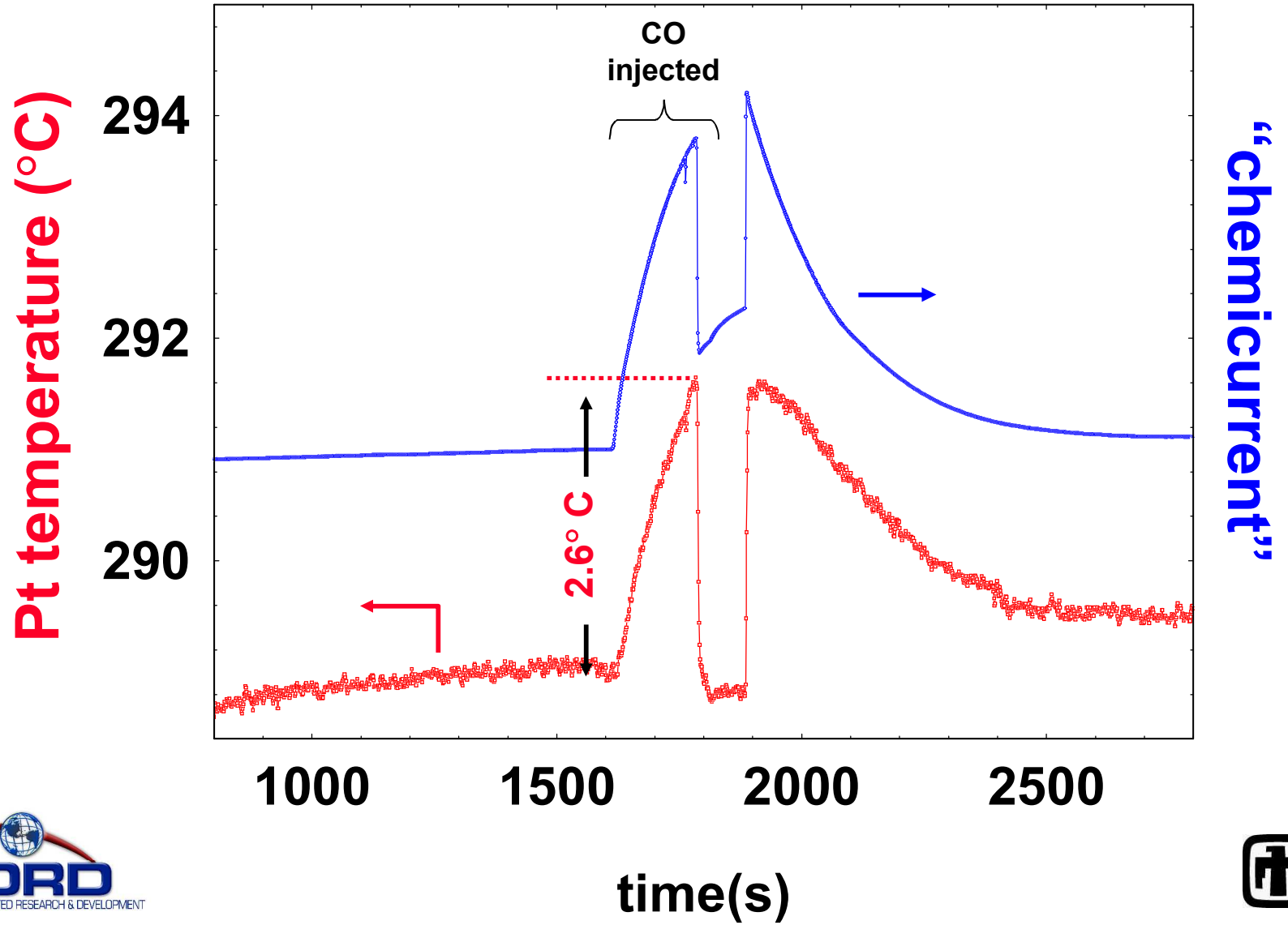
Experimental methods of temperature measurement

Nanodiode mounted with thermocouples on contacts



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



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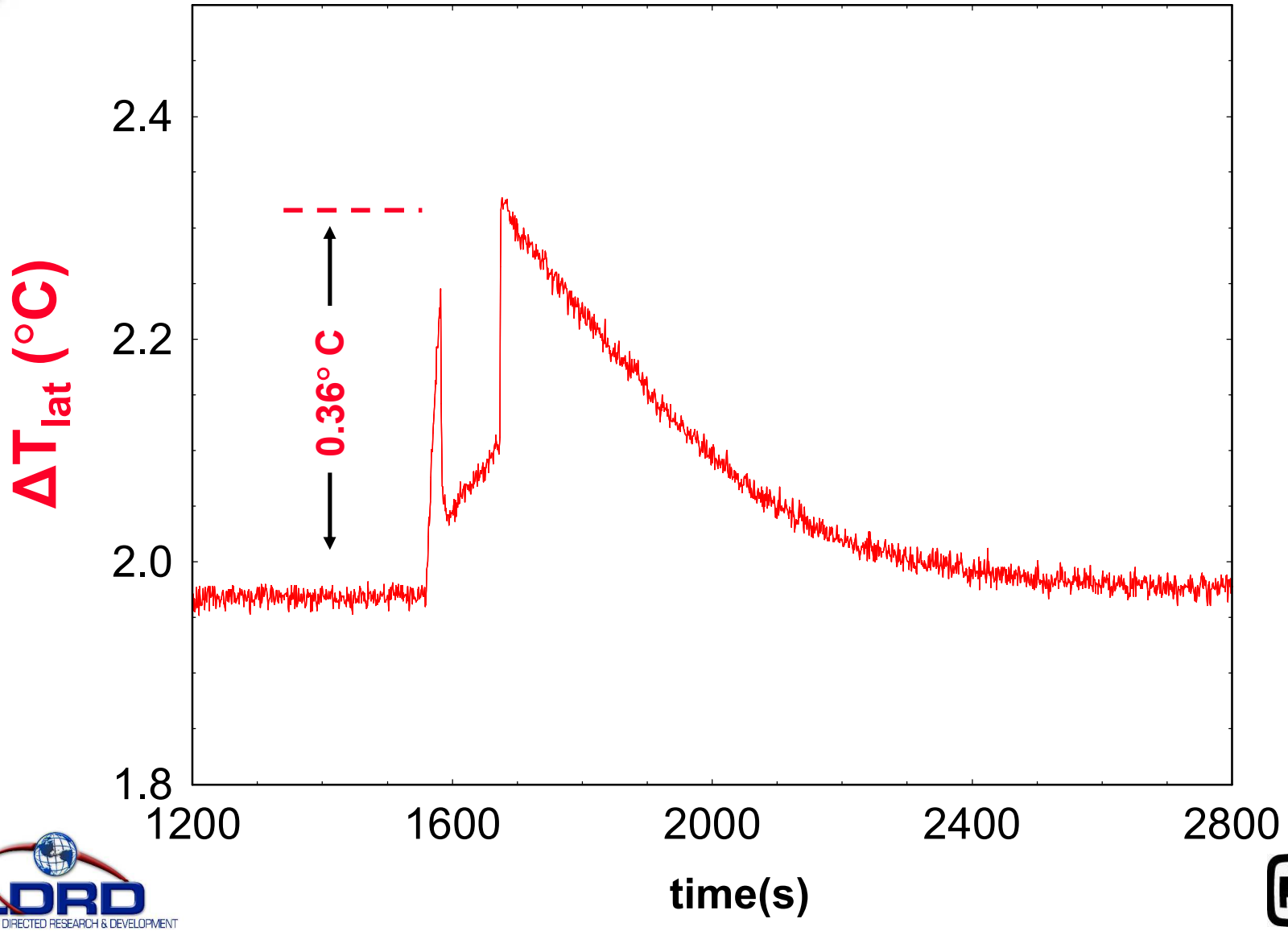
thermocouples are used to measure the lateral temperature gradient during reaction



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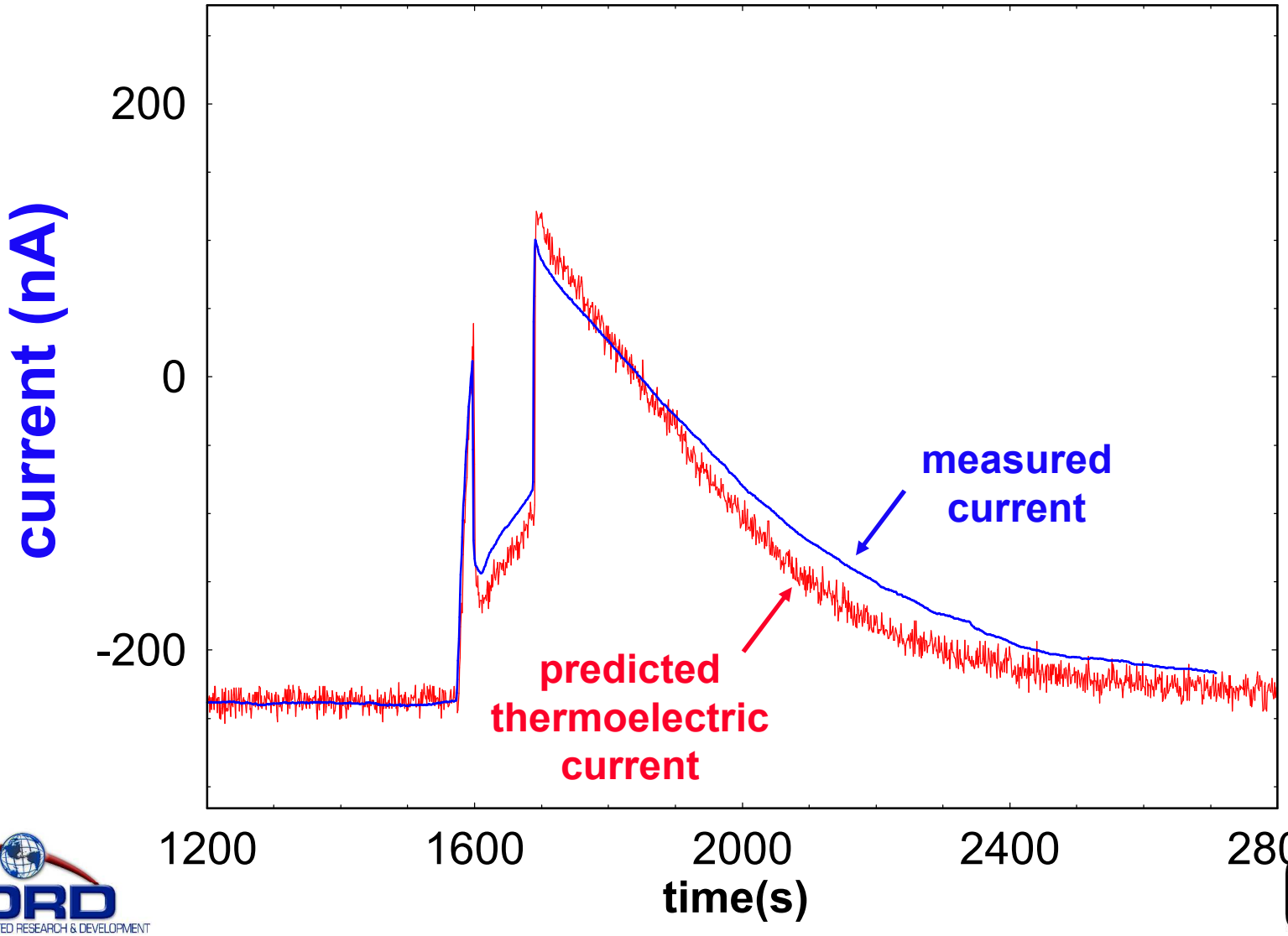
Observed current can be quantitatively explained using ΔT_{lat} , the Seebeck Coef, and the diode resistance, it is entirely due to thermoelectric voltage



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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 only considered the vertical temperature gradient within the thin Pt and TiO_2 layers ($\Delta T_{\perp}$), which significantly underestimates the temperature changes from the reaction exothermicity

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