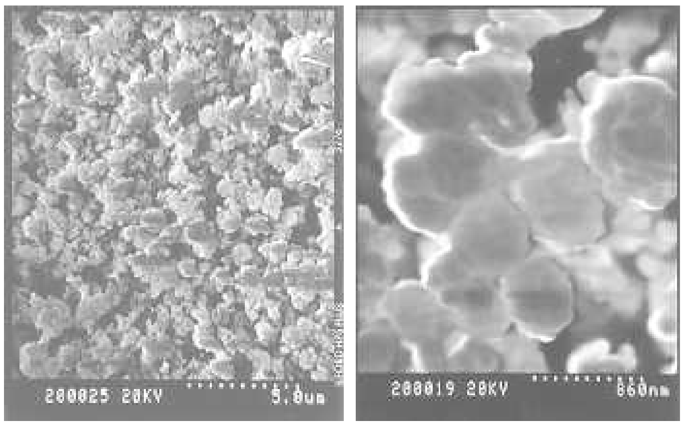
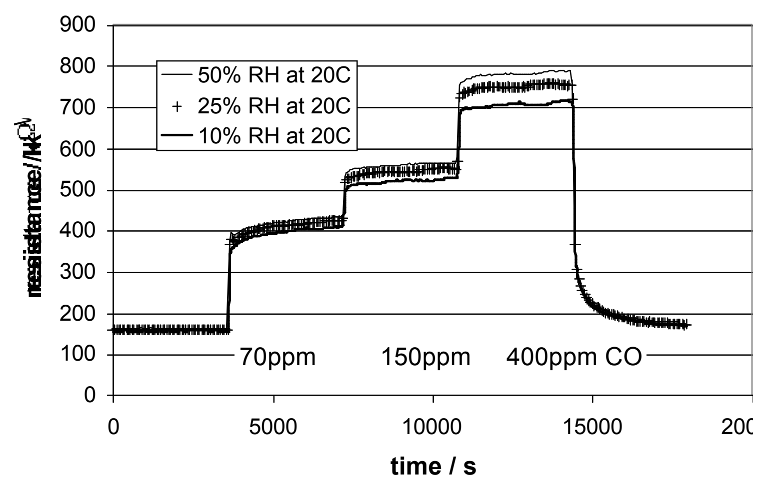
The electrical interaction between the catalyst surface and the target gas molecules



Dirk Niemeyer

Berlin 21.11.03

Response of thick-film sensor device operating at 400°C, in atmospheres of different relative humidity



Semiconducting oxides as elevated-temperature gas-sensitive resistors

- Adsorbed oxygen or surface oxygen vacancies act as electron or hole trap states
- Variation in the surface concentration results in a strong conductance variation
- Variations caused by reaction with trace gases in the atmosphere.
- Detect ppm concentrations of carbon monoxide, hydrocarbons, H_2S, NO_2 etc
- Detect ppb concentrations of O_3

Materials technology for oxide gas sensors

- SnO_2 commercialised in 1960s (Taguchi: Japan): big effects of water vapour
- Demonstration that effect is common for oxides (1982-85 at Harwell)
- Capteur Sensors started 1992 from UCL / Harwell
- $Cr_{2-x}Ti_xO_3$ (solid solution with $x<0.3$) introduced for CO, hydrocarbons (1994-9)
- WO_3 introduced for O_3 (1994-9)

Generality of behaviour

- Almost any oxide will be a gas sensor if it is prepared as a sufficiently finely porous body that surface states dominate the conductivity

  – In general, oxides show very similar patterns of behaviour to one another: there is not in general any pattern of very different responses to chemically different gases
  – Behaviour must be mediated by a chemical species common to the surface of all oxides

- P T Moseley, A M Stoneham and D E Williams in "*Techniques and Mechanisms in Gas Sensing*", Ed P T Moseley *et al*, Adam Hilger, Bristol, 1991

Thermodynamical aspects

$DG=DH-TDS$

Chemisorption ideal if $T\Delta S < \Delta H$ e.g. at $T=0K$

Point defects ideal if $T\Delta S > \Delta H$ e.g. at high T

Screening of the sensor response,if not affected by gas composition

Best gas response was obtained between 200 and 600 ^{o}C

Kinetic aspects

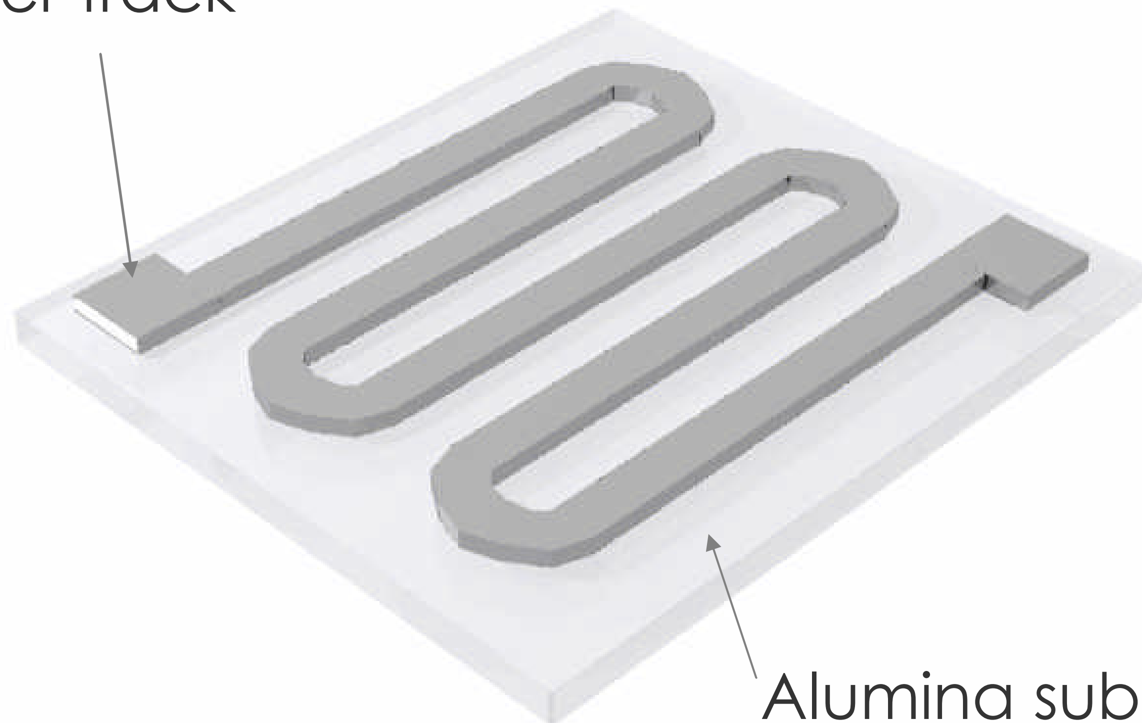
$$\frac{1}{2}\,O_2 + 2n' \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_{ads}^{2-}$$

$$CO + O_{ads}^{2-} \xrightarrow[k_2]{} CO_2 + 2n'$$

Surface trap state density, N_S is sensitive to CO partial pressure, P_{CO} , if $k_2 \gg k_{-1}$ and k_1.

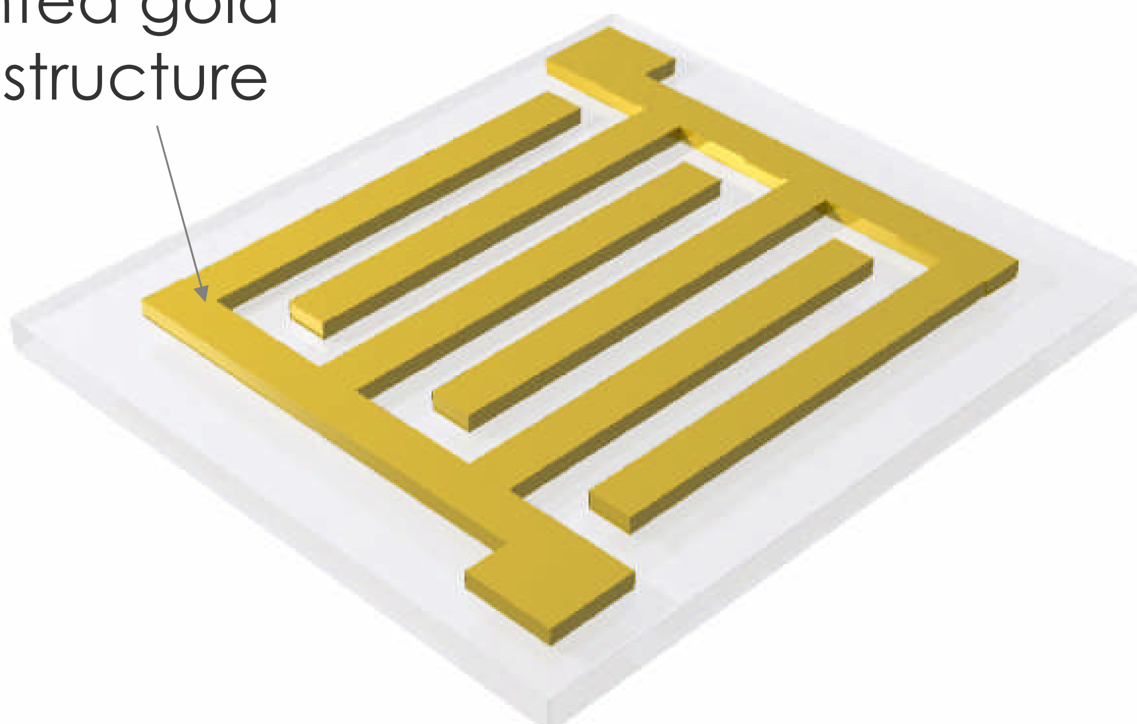
Oxygen adsorption creates an electron trap state in the oxide band gap. Reaction with the gas removes the state

Sensor Fabrication



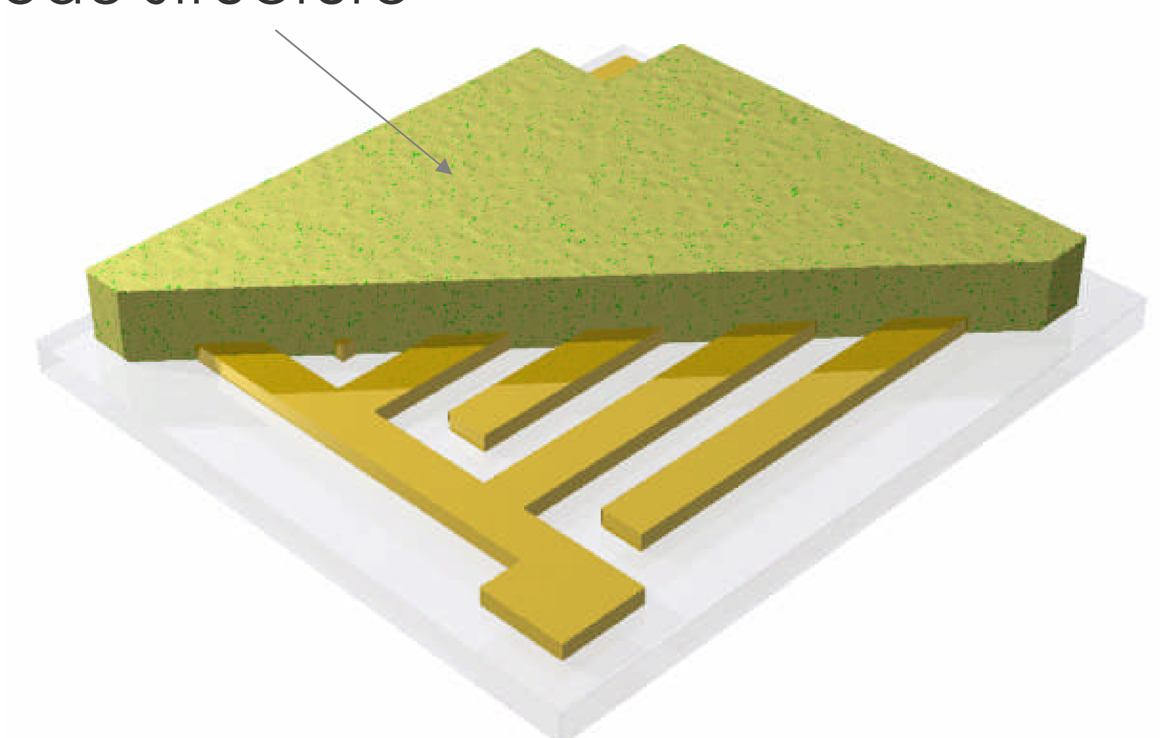
Sensor Fabrication

Screen printed gold
electrode structure

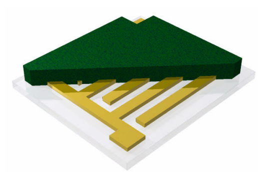


Sensor Fabrication

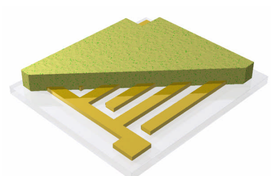
Sensing oxide deposited onto electrode structure



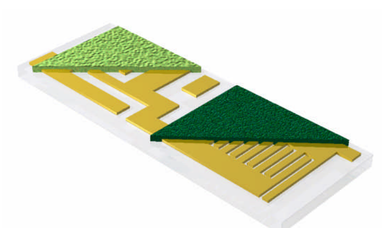
Sensor Product Range Includes



- Chromium Titanium Oxide (AA,G,CT)
  - Operated at 350 ^{0}C, 400 ^{0}C and 475 ^{0}C
    - Detects ***Reducing*** gases such as Carbon Monoxide, Air Quality, Ammonia, Hydrocarbons, Hydrogen Sulphide, Sulphur Dioxide

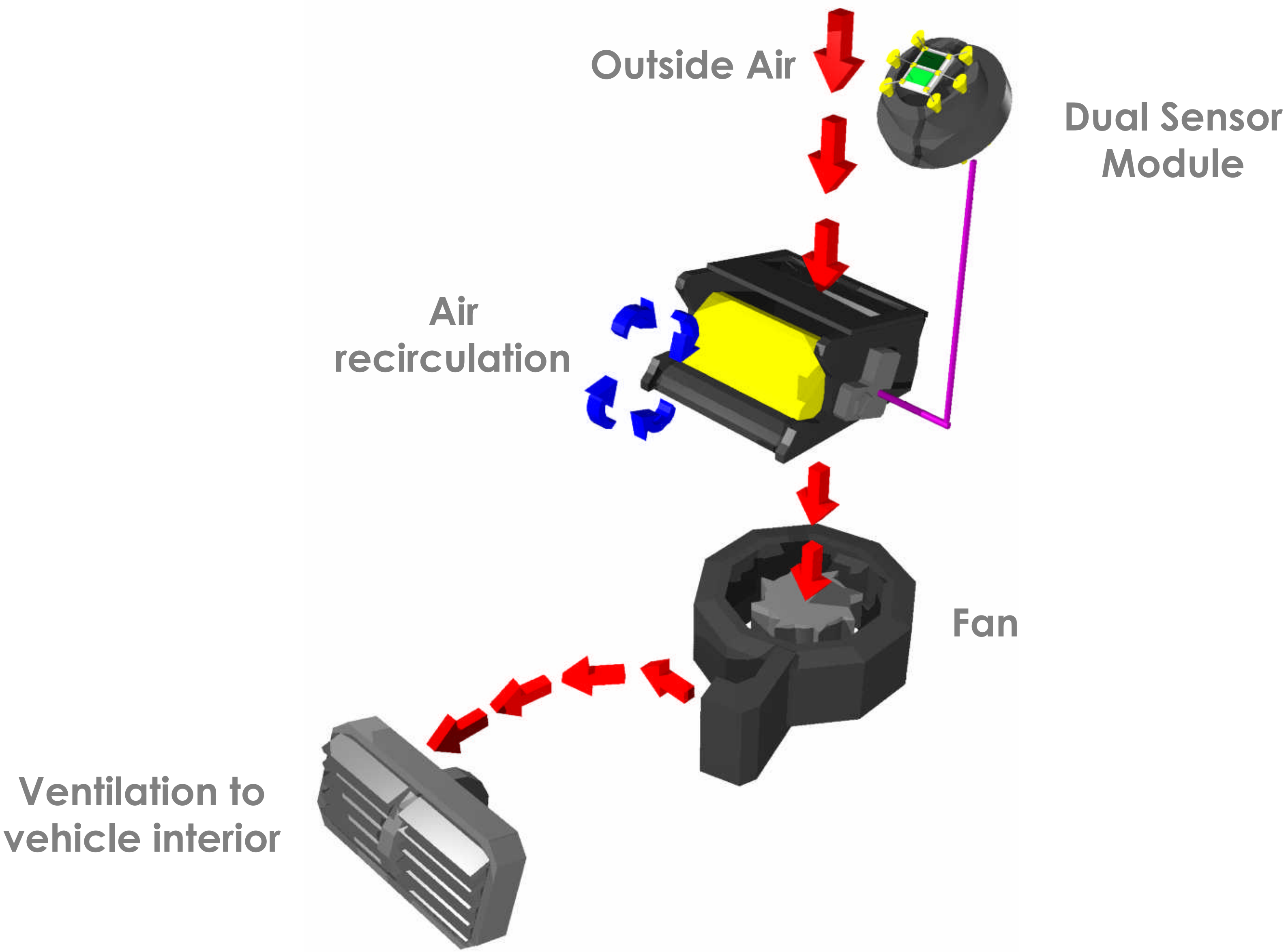


- Tungsten Oxide (LG)
  - Operated at 400 ^{0}C and 500 ^{0}C
    - Detects ***Oxidising*** gases such as Ozone, Nitrogen Dioxide and Chlorine

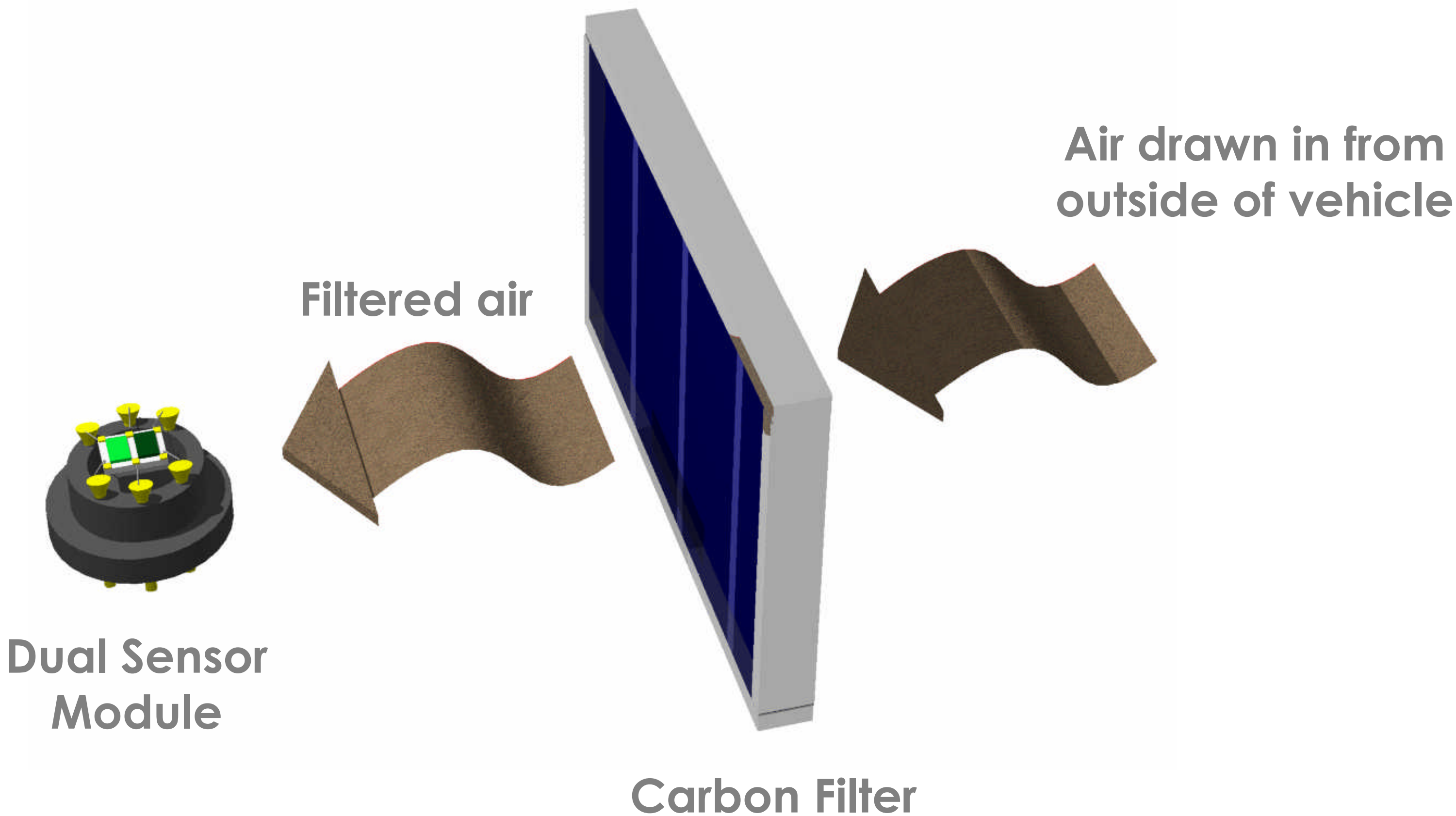


- Dual Sensor
  - Operated at 400 0C
    - Separate detection of both Reducing and Oxidising gases on a single chip

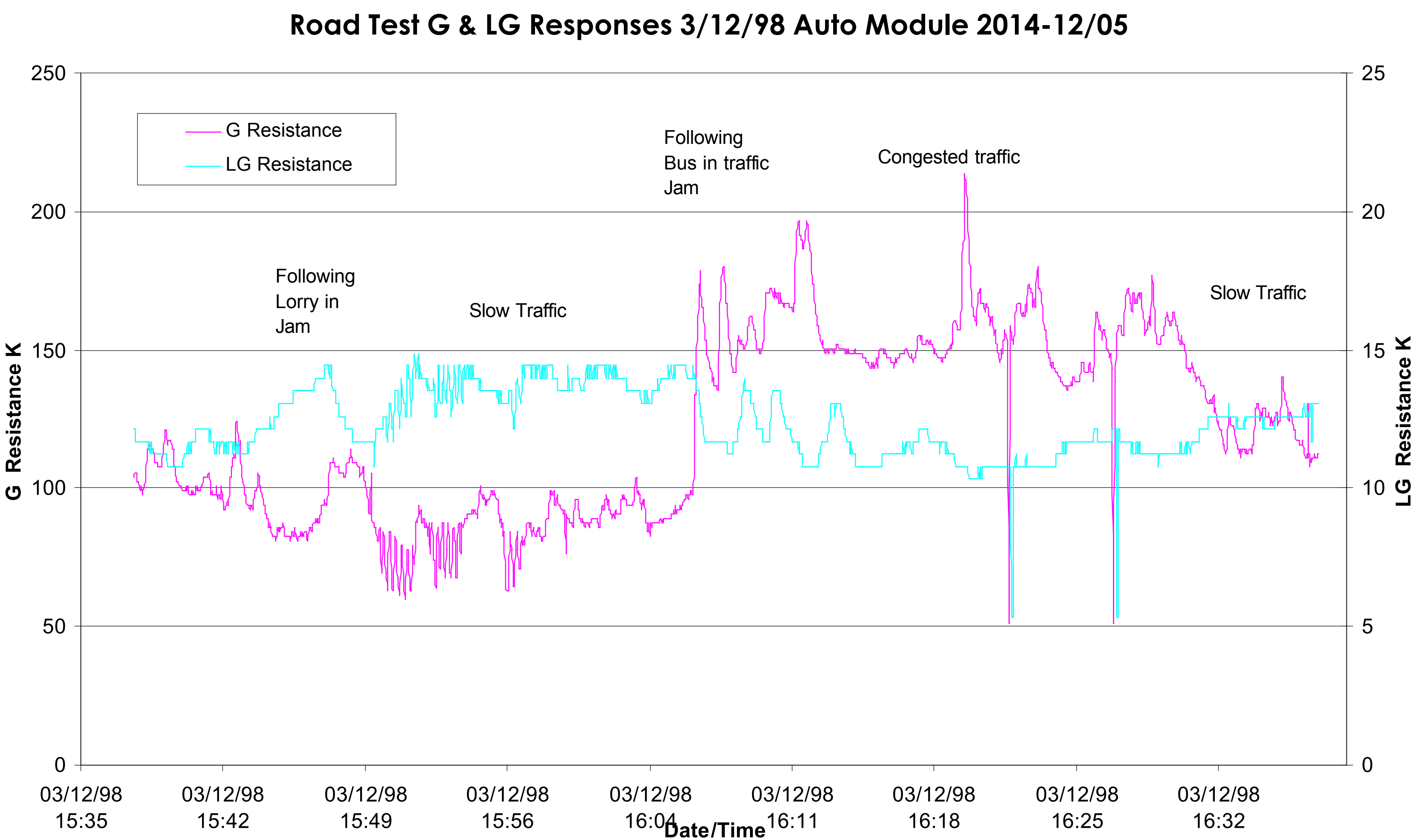
Automatic Air Recirculation



Carbon Filter Service Life



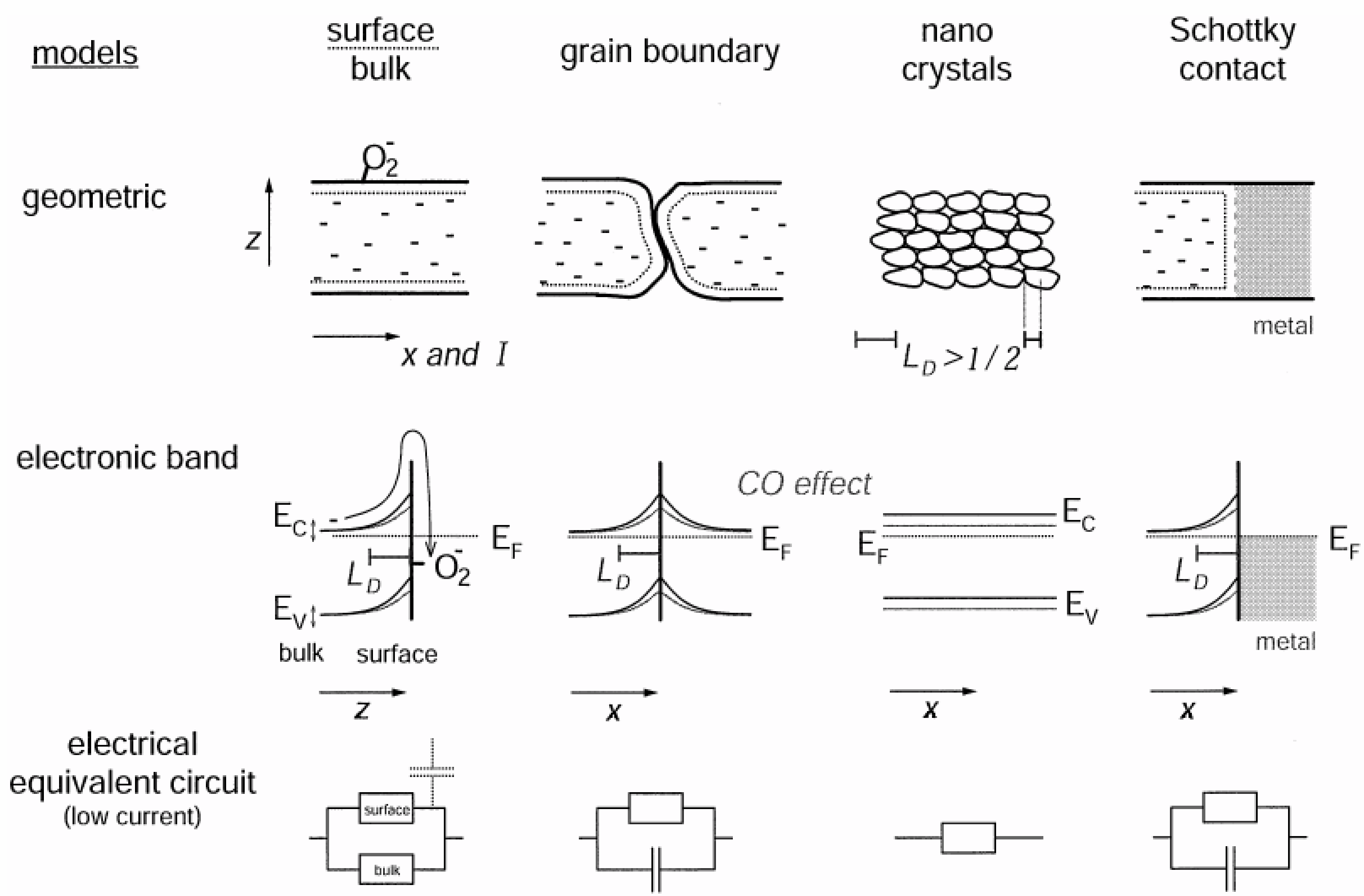
Air Quality Module (Automotive)



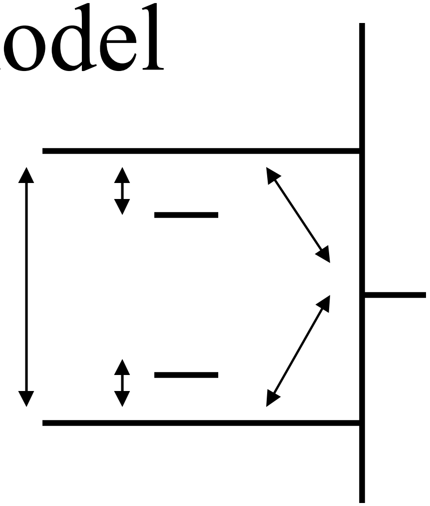
Objectives

- Understanding behaviour of real structures from microscopic models
  - Modelling effect of microstructure on behaviour
- Understanding the surface chemistry that couples to conductivity change
- Improving performance of practical devices
  - Reducing operating temperature
  - Reducing water vapour effects
  - Understanding and eliminating drift

Microstructure effects



Surface trap-limited model



D E Williams and P T Moseley, *J Materials Chem* 1 (1991) 809-814

D E Williams, *Sens Actuators B*, 57 (1999) 1-16

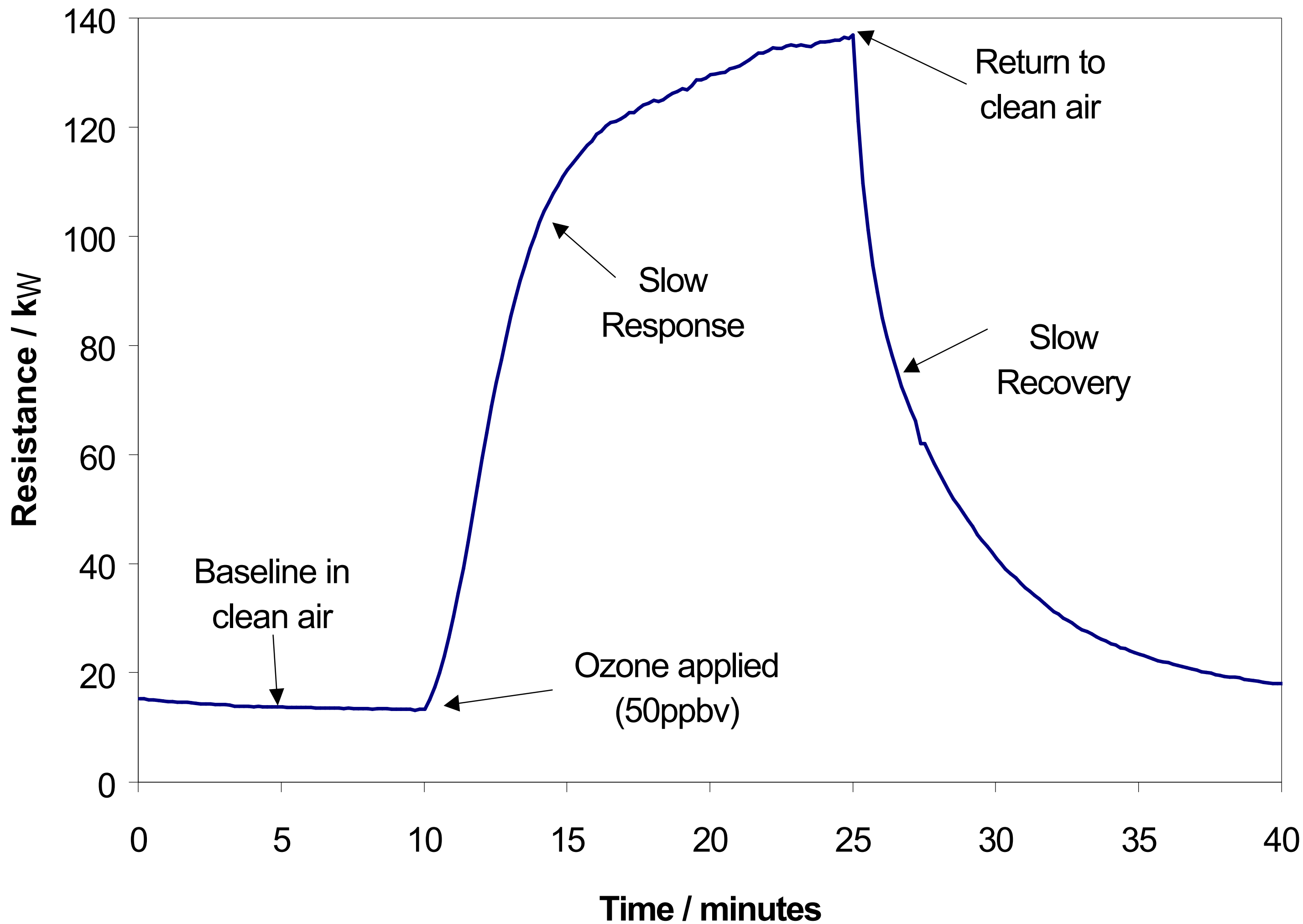
'Flat band' approximation

Equilibrium of surface state, bulk acceptors and donors, conduction and valence band
Porous solid treated as homogeneous

Gas sensitivity from decrease of surface acceptor state density with increase of gas concentration

'n' type (resistance decrease with reducing gas) or 'p' type (resistance increase with reducing gas) depending on bulk donor density

Typical Ozone Sensor Response



Why measure O_3 with a WO_3 sensor?

- O_3 measurements required in stratosphere, troposphere and for indoor air quality determination
- Present instrumentation is expensive and bulky
- WO_3 based sensors are
  - Sensitive in ppb range
  - Selective for O_3
  - Small and light
  - Cheap

Response Model basics

- Conductivity controlled by oxygen vacancies.

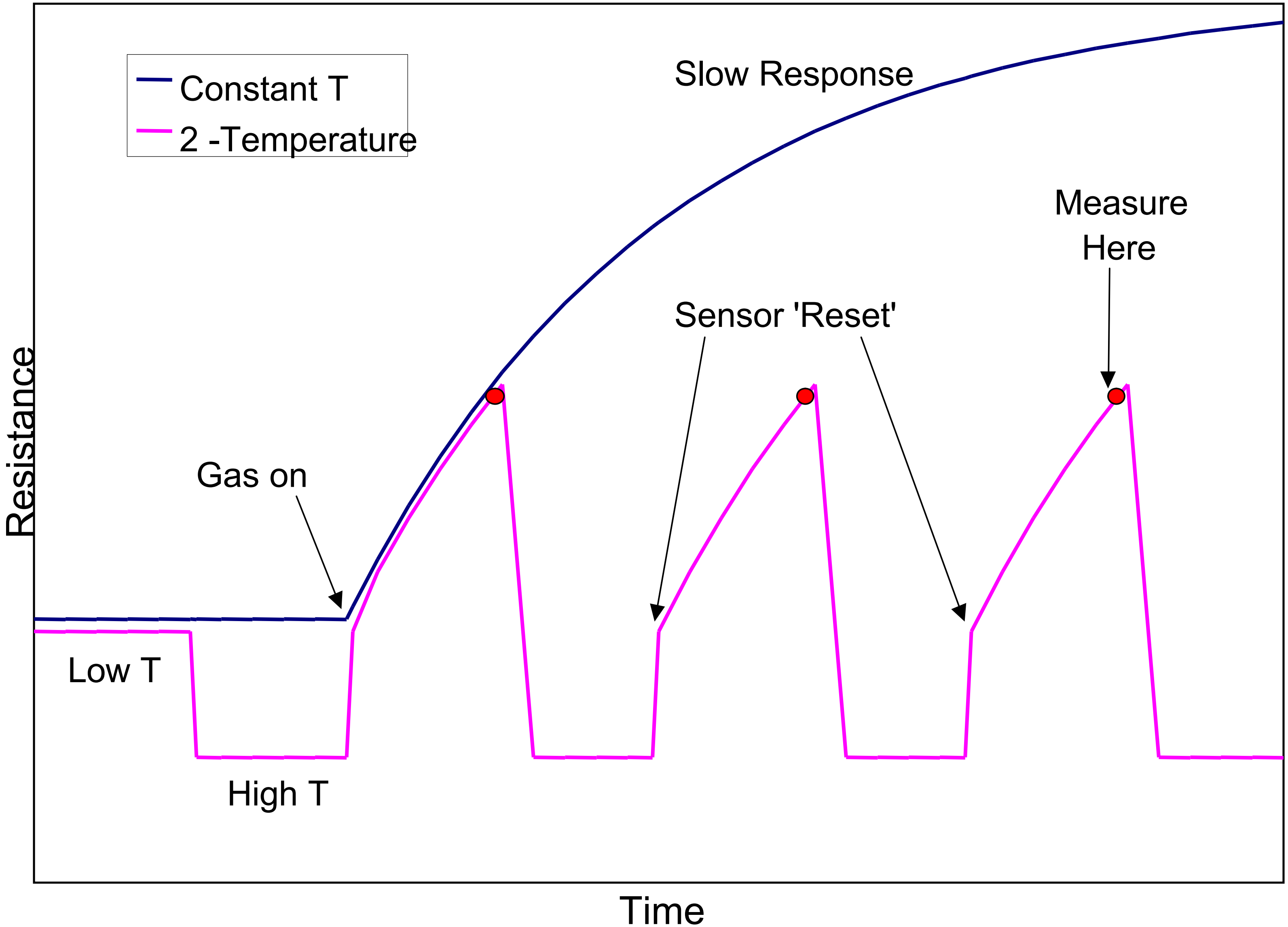
$$X \underset{k_{-1}}{\overset{k_1}{\longleftrightarrow}} V + \frac{1}{2}O_2 \qquad V + O_3 \xrightarrow{k_2} X$$

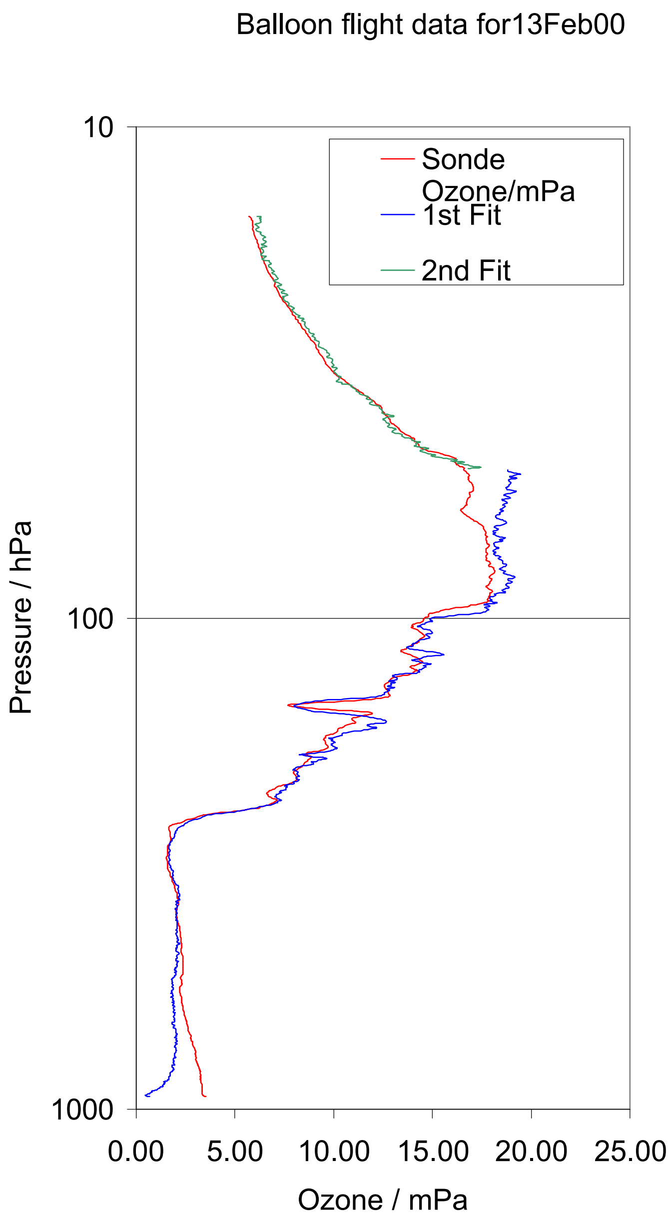
X = unperturbed lattice
V = neutral species (ion pair of oxygen vacancy + reduced lattice tungsten ion)

- Charge carriers produced by thermal excitation of electrons from reduced tungsten ions into the conduction band.

Charge carrier and therefore conductivity changes in response to changes in oxygen vacancy concentration at the interface (determined by $[O_3]$).

Two-Temperature Operation



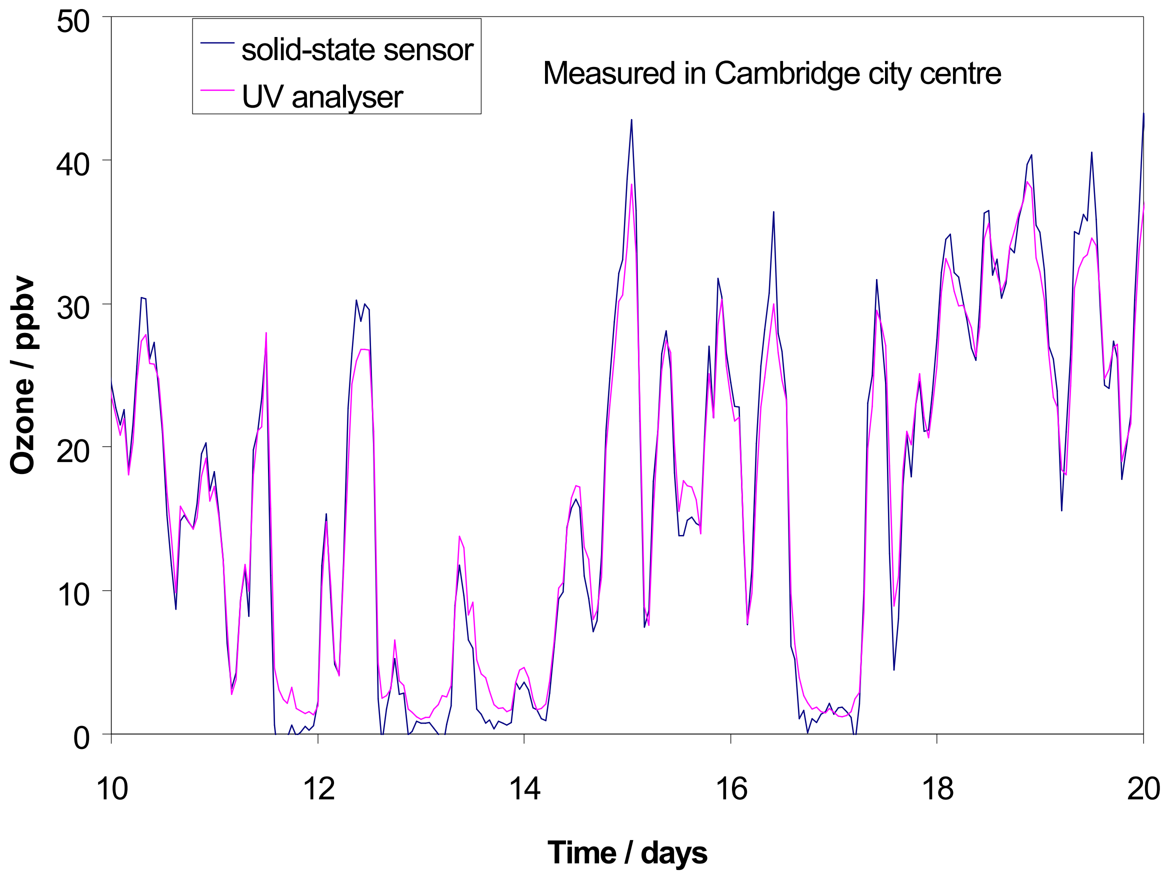


Balloon Flight

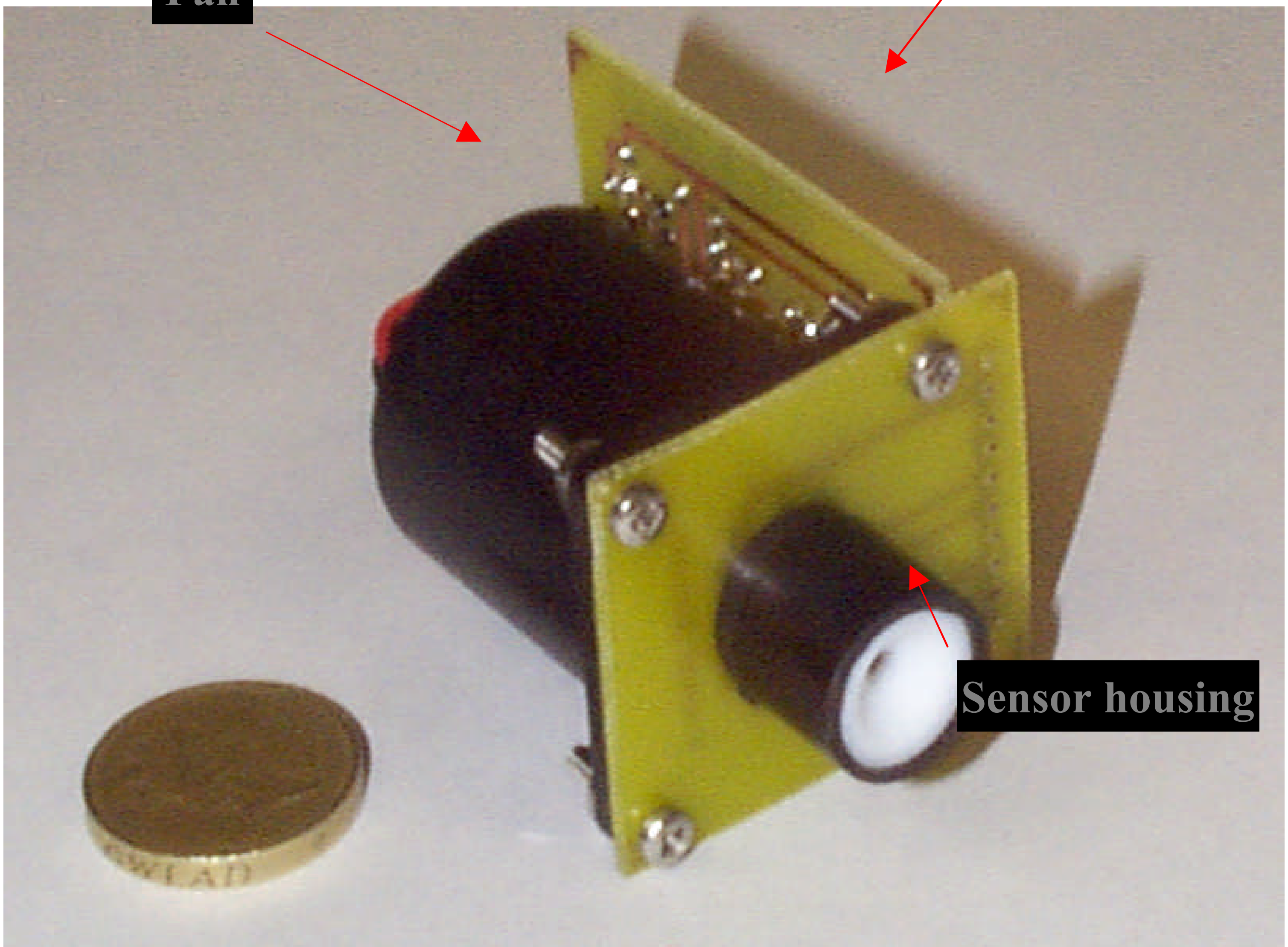
Ozone sensor response compared to ozone sonde.

Sensor response is scaled to fit

Comparison with commercial Instrument



Ozone Instrument - Sensor / fan module



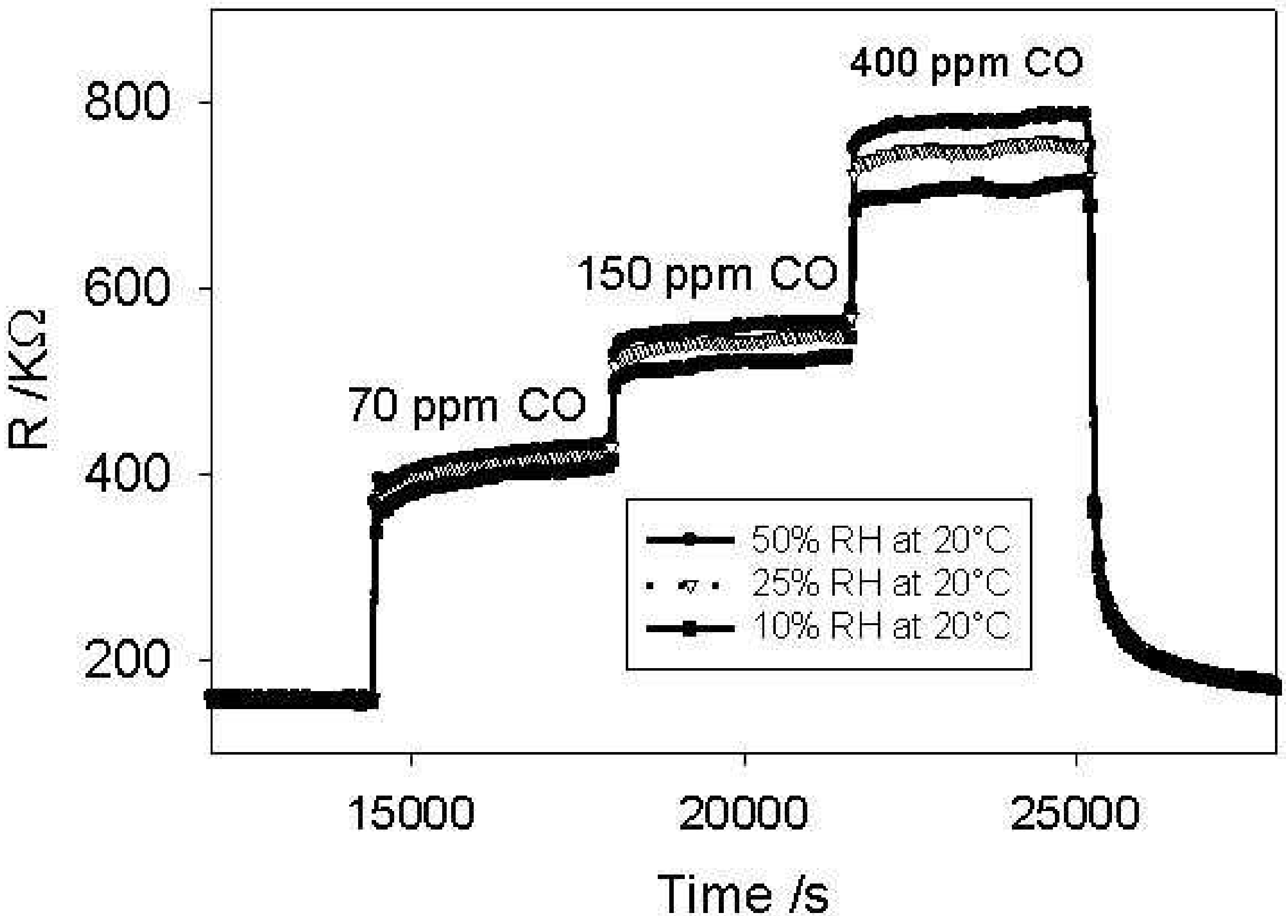
Challenge for theory

- Ozone reaction with vacancies
  - Why is it slow on WO_3
  - Dependence on nature of vacancies and other surface sites
- Slow ozone decomposition on WO_3
  - (allows device based on thick porous layer running at 500^{o}C to work!)
- Vacancy migration in WO_3 and effect of surface electric field

$Cr_{2-x}Ti_xO_3$: new ‘reducing gas’ sensor material

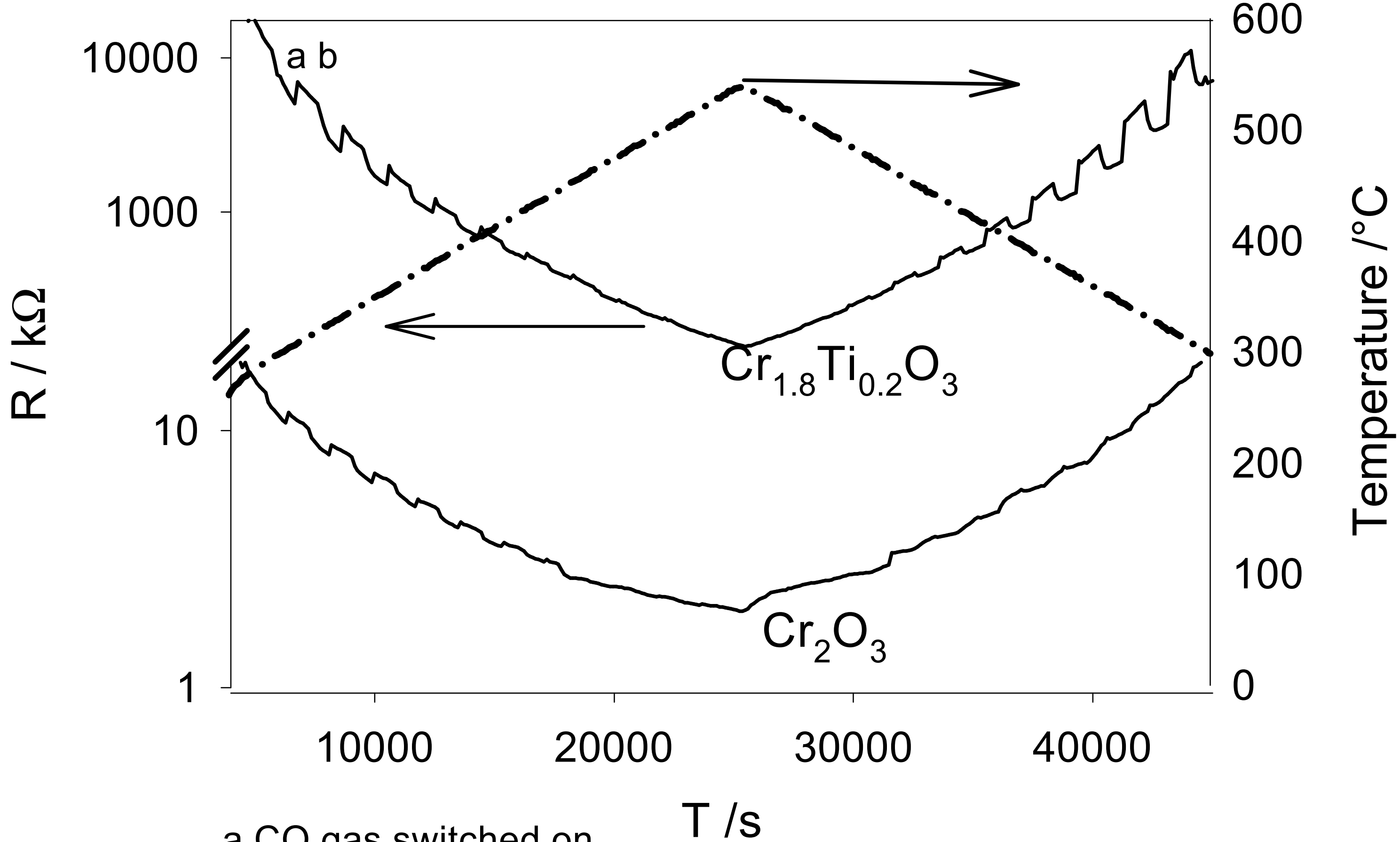
- Robust and resistant to poisoning
- Stable in low oxygen partial pressure
- Small effect of water vapour

Influence of water vapour



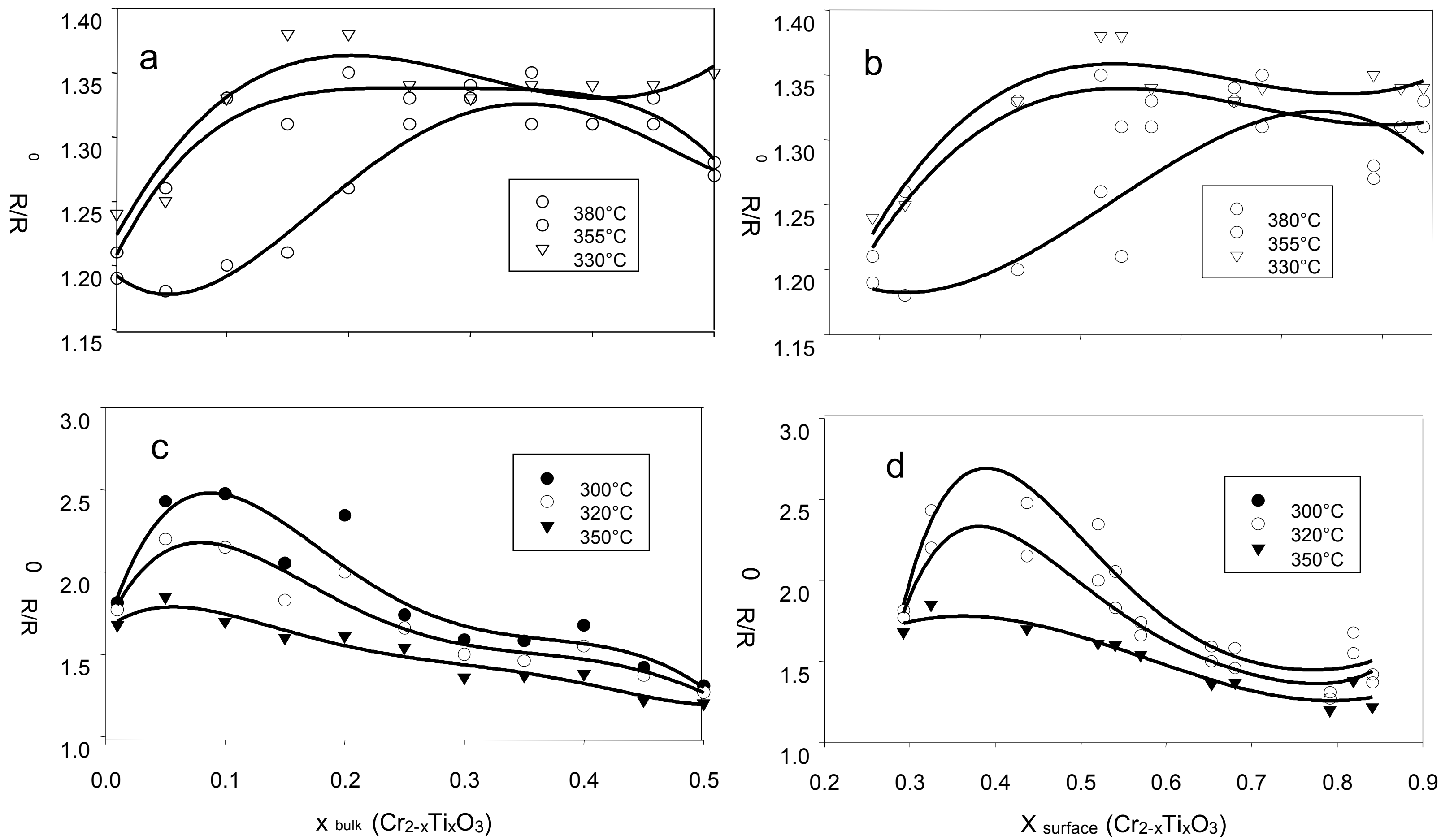
Chromium titanium oxide: $Cr_{2-x}Ti_xO_3$; $0.01 < x < 0.4$

Temperature effect

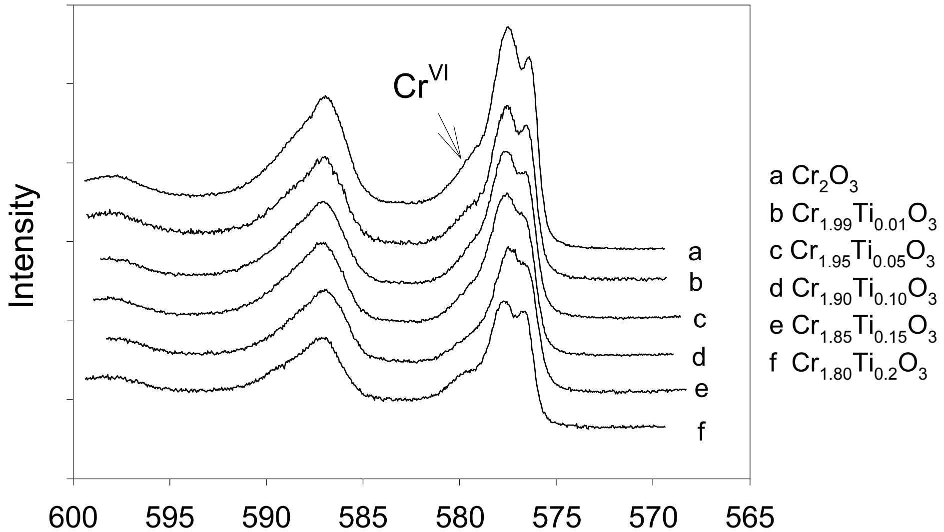


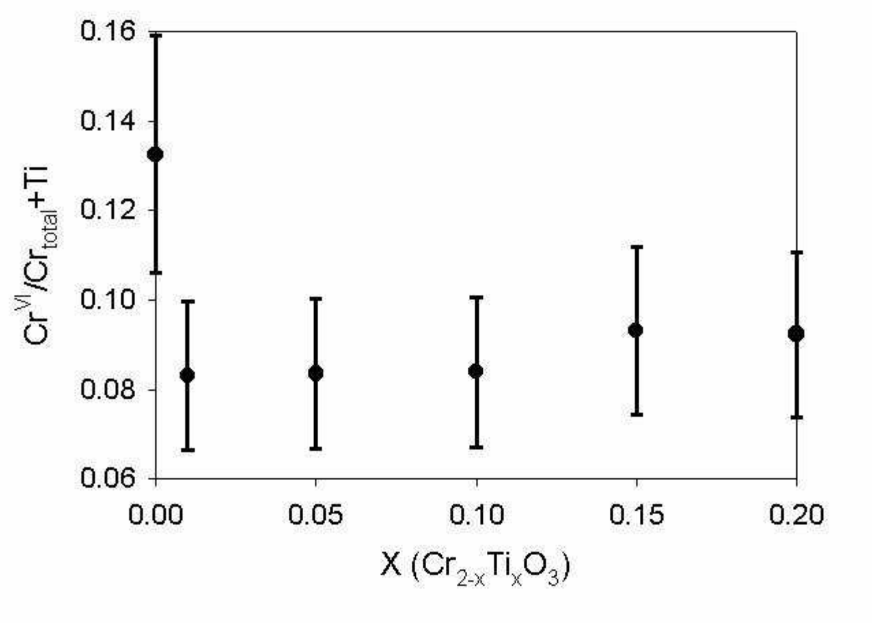
a CO gas switched on
b CO gas switched off

Gas response to 500 ppm of CO

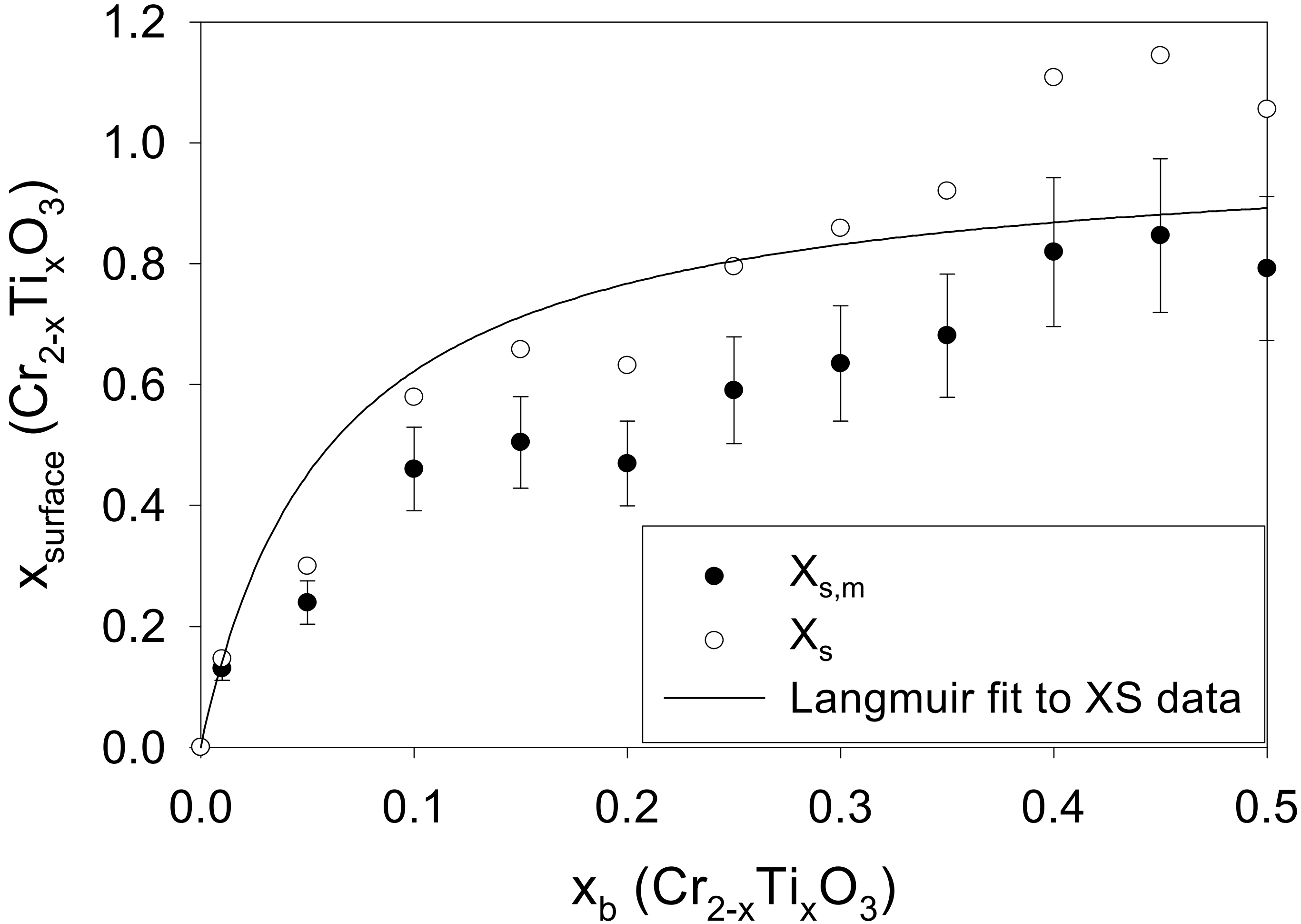


Surface Cr(VI) ‘neutralised’ by Ti substitution





Ti surface segregation controls sensor effect



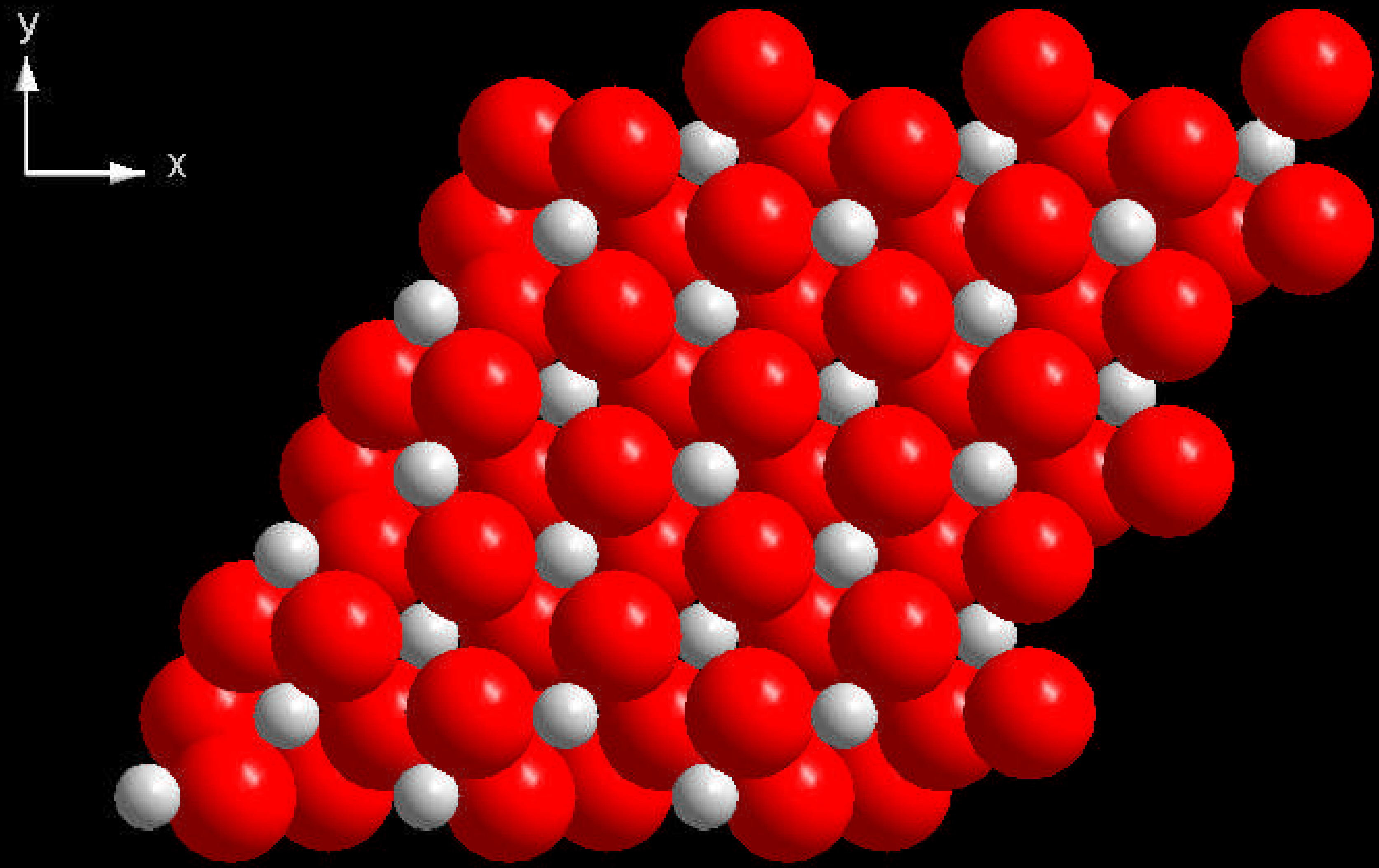
Defective Cr_2O_3 and CTO

$$Cr_2O_3 \rightarrow Cr^{3+}_{2-2x}Cr_x^{6+}O_3$$

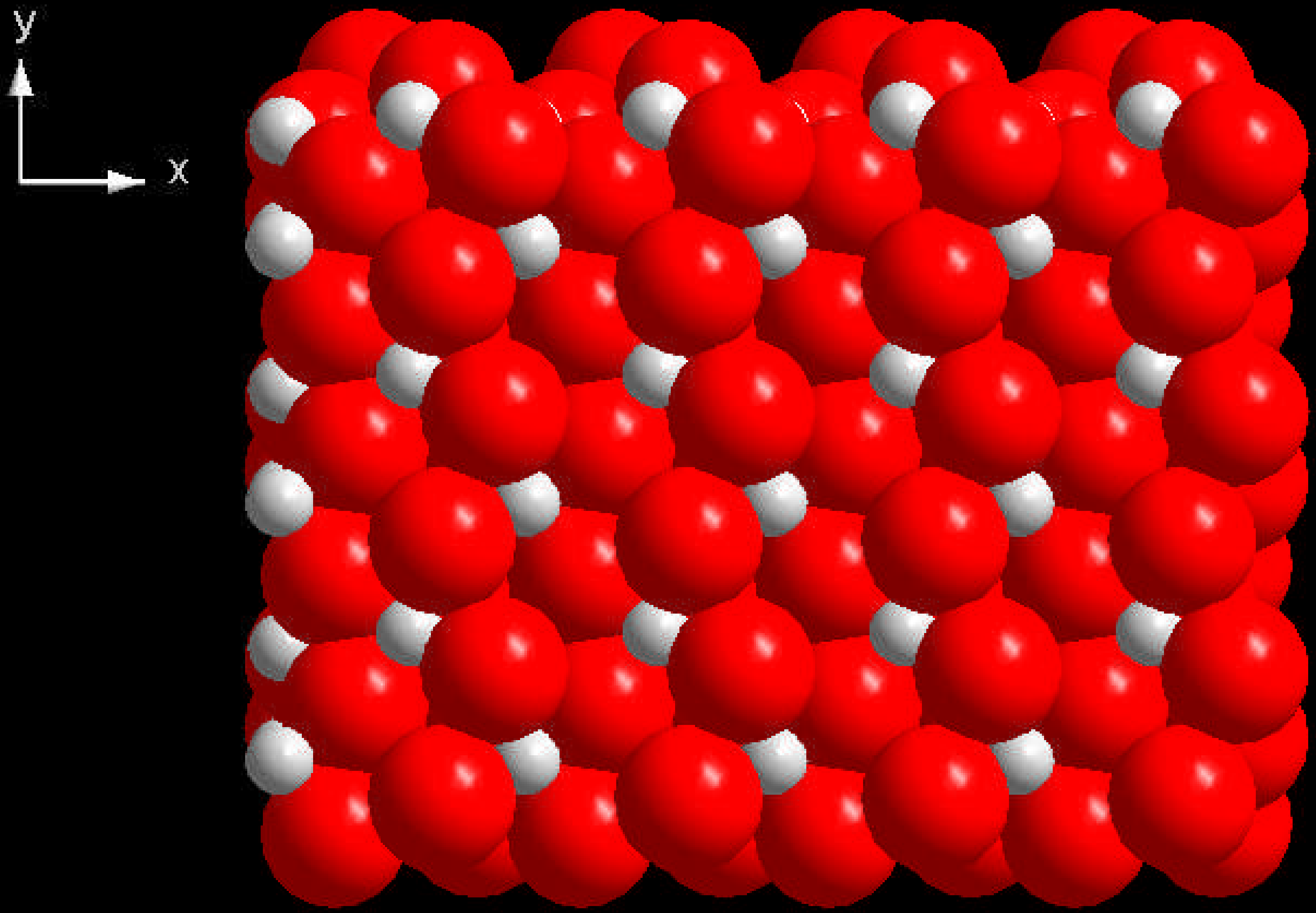
$$\left[1-\frac{2x}{3}\right]Cr_2O_3 + xTiO_2 \rightarrow Cr_{2\left(1-\frac{2x}{3}\right)}Ti_xO_3$$

Holt, A. and Kofstad. P., *Solid State Ionics*, **117** (1999) 21

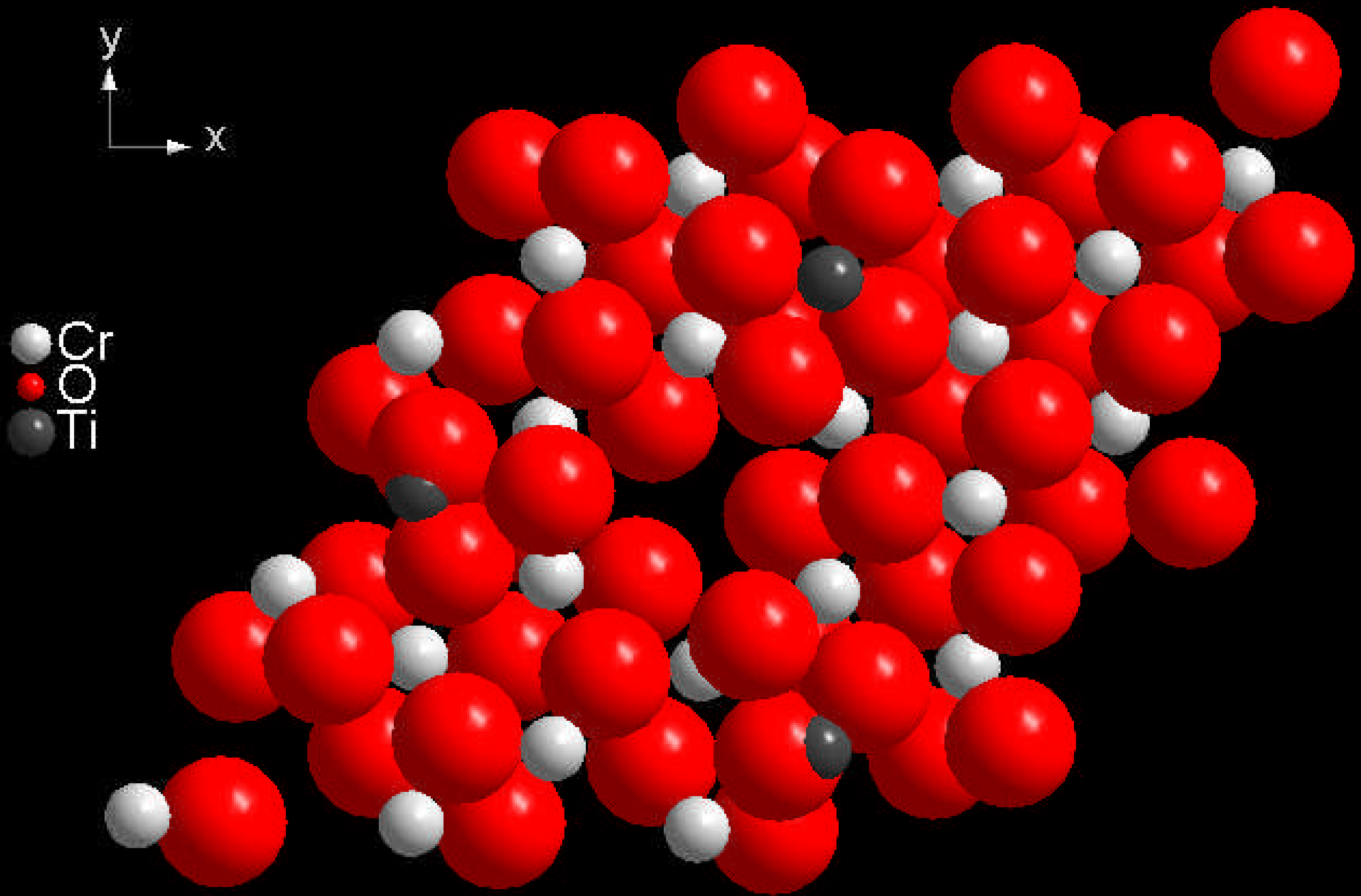
0001 face



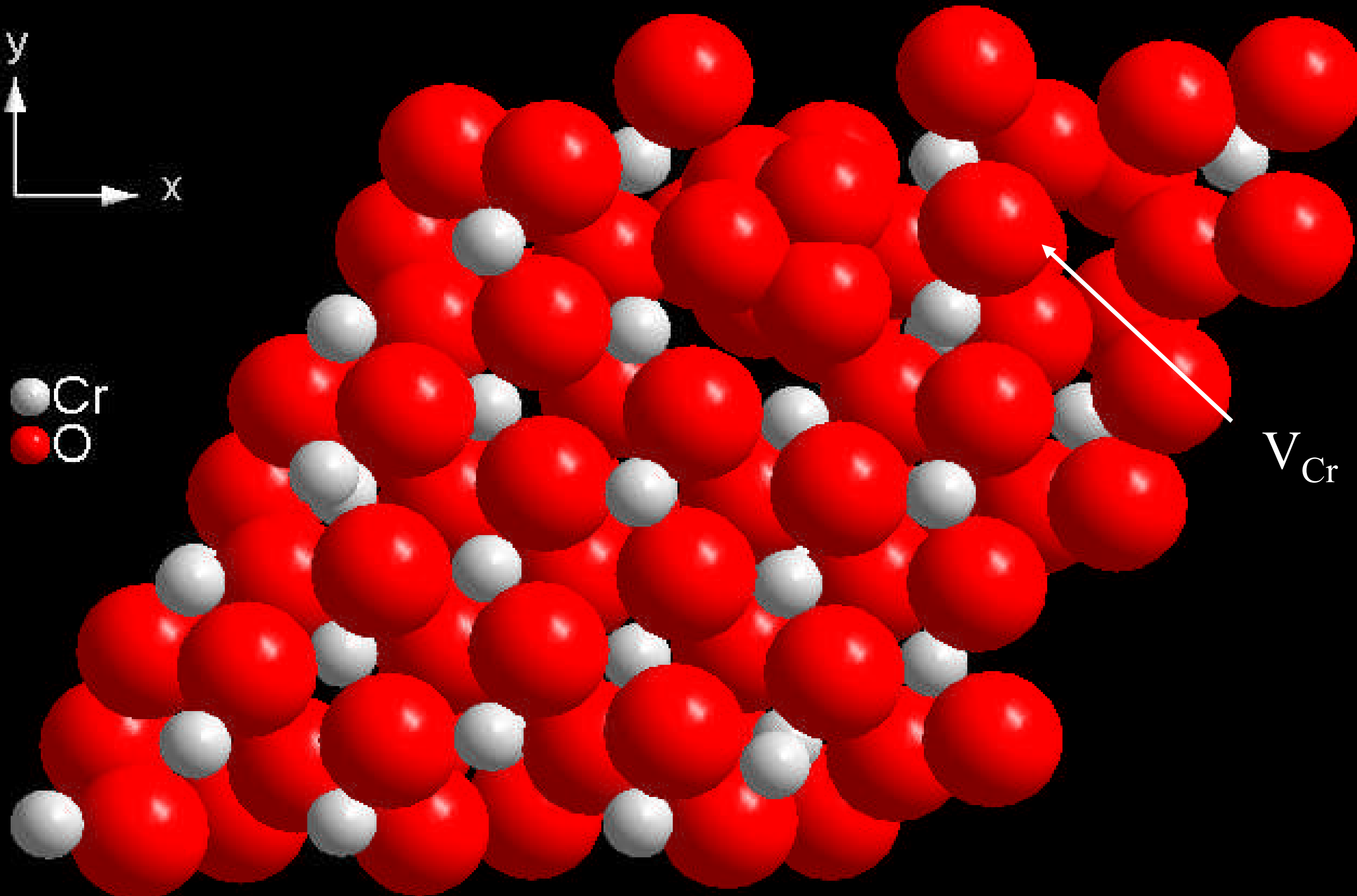
$10\bar{1}2$ face



Ti_3V_{Cr} defect cluster



Cr^{VI} /V_{Cr} defect Cluster



Why Ti substitution in Cr_2O_3 develops gas response

- $Cr^{(VI)}$ acceptor state surface segregated
  - Charge balanced by Cr vacancies
  - Large carrier concentration near surface
  - Masks effect of surface oxygen acceptor states
- $Ti^{(VI)}$ is surface segregated
  - Charge balanced by Cr vacancies
  - Neutralises Cr(VI)
  - Decreases surface carrier concentration
  - Unmasks effect of surface oxygen acceptor states

Hypothesis: Mars and Van Krevelen mechanism for gas response

$$\mathbf{M_{surf} + CO \rightarrow [M{:}CO]_{surf}}$$

$$\mathbf{[M{:}CO]_{surf} + O_{latt,\ surf} \rightarrow M_{surf} + V_{O,\ surf} + CO_2}$$

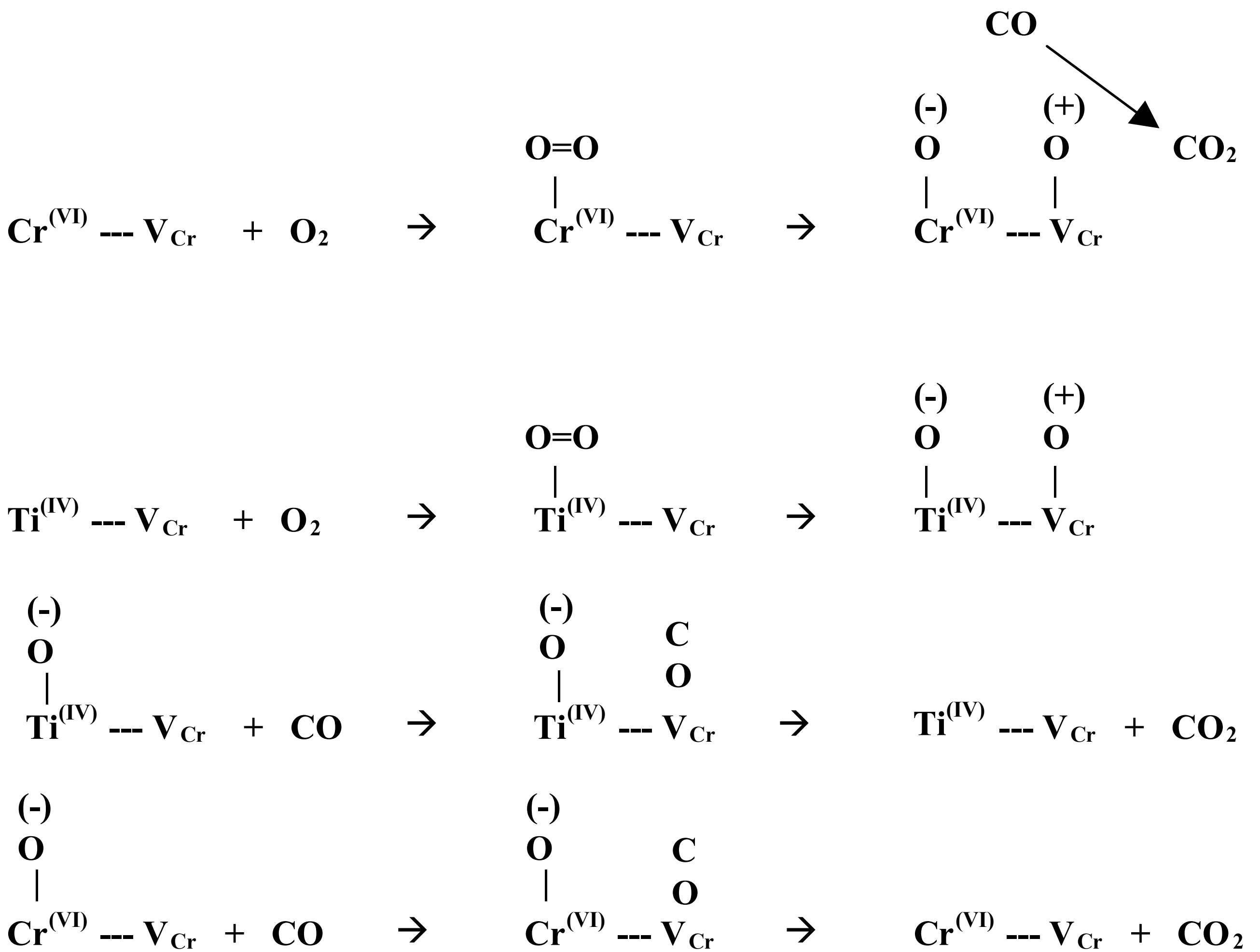
$$\mathbf{V_{O,surf} + O_2 \rightarrow O_{latt,surf}}$$

A general mechanism assumed for redox catalysis on transition metal oxides.

Hypothesis from computational modelling

Distortion of surface oxygen arrangement creates a binding site for gases; high valence cations make dissociation sites for oxygen and water.

Scheme 1: Model for surface processes. Reactions A create reactive oxygen species which can also act as surface trap states for electrons. Reactions B remove the reactive surface oxygen species. Reactions C regenerate the initial surface state.



(B)

(A1

(A2

(C1

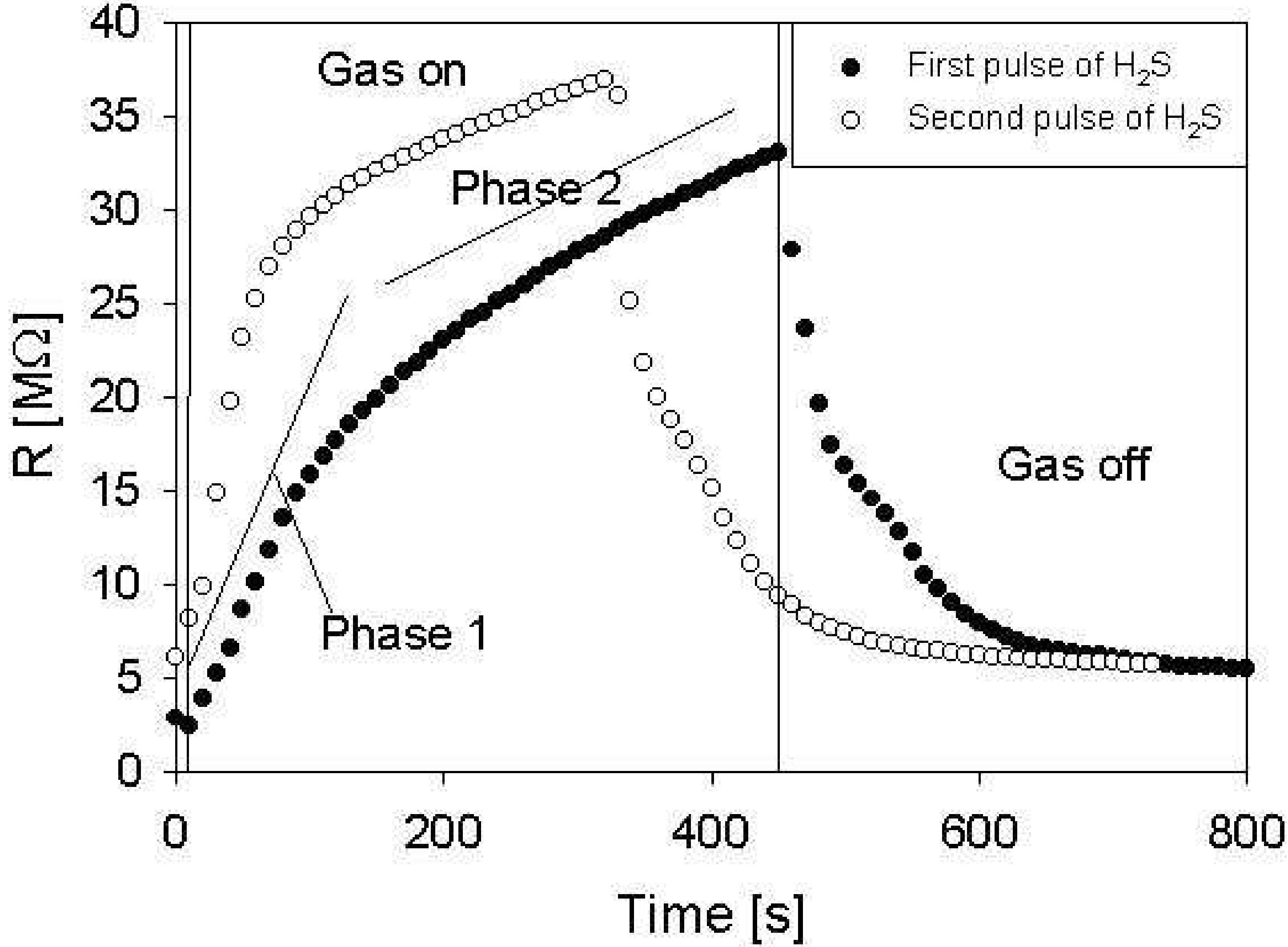
(C2

Gas-sensor measurements as a probe of surface sites of oxides

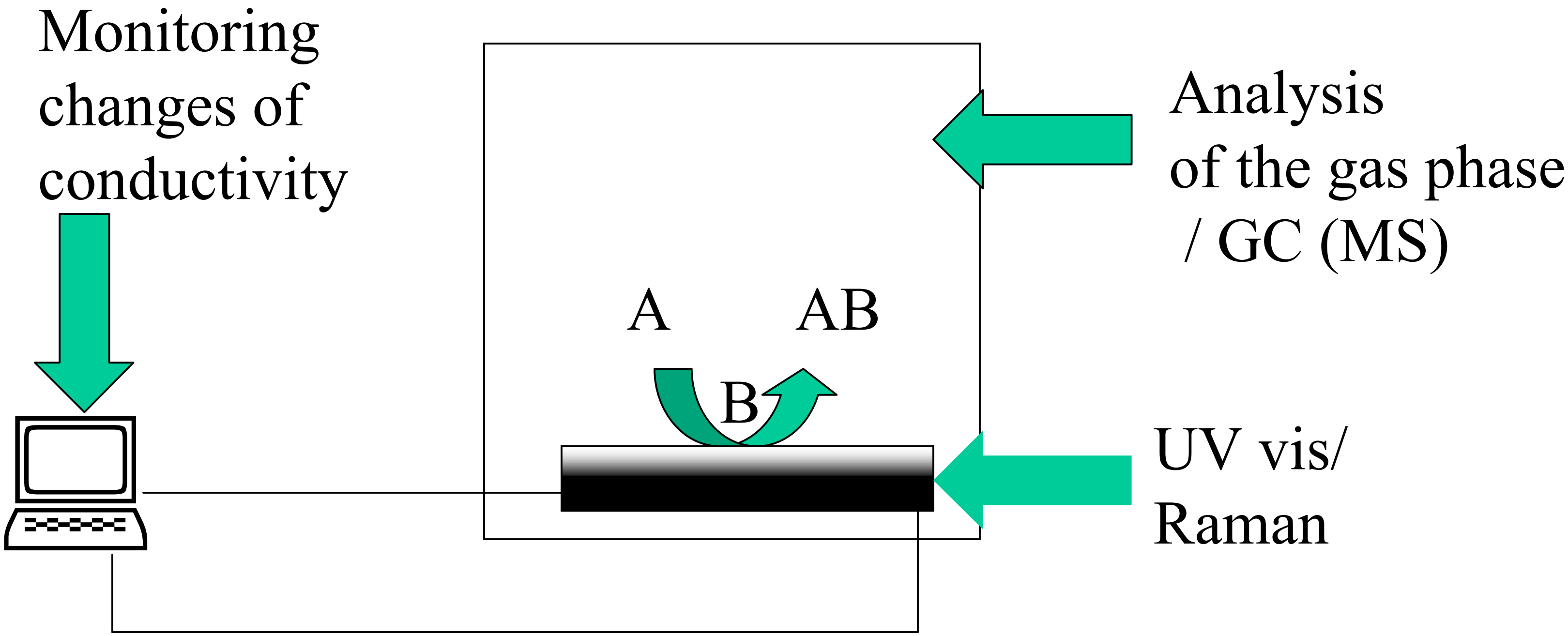
- Surface conditioning (‘poisoning’)
  - sulfur dioxide, H_2S → reversible sulfation
  - Siloxane HDMS → irreversible silication
  - Carbon dioxide, aldehydes → reversible carbonation
- Surface segregation

Affect subsequent response to different gases and to water vapour in different ways

Discriminating surface sites by poisoning



In situ setup (ideal experiment)



Is it possible to correlate these phenomena???

Acknowledgement

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