A Modeling Tentative of Operation of Gas Sensor through Atomic Scale Insights

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Gassensing based on metal oxide sensing layer

**Measure of conductivity**

Variations come from **electronic transfers** caused by **reactions** occurring at the surface of the sensing layer due to the target gas &

Transformation of those charge transfer processes into **measurable changes** in electrical resistance of the sensing layer

To push forward sensor development: nanostructuration, doping ... 
Answers provided during this meeting!

- Molecules adsorption on the surface of the sensing layer
- Charges transfers btw surface species and Oxide
- Concentration of adsorbed or formed specie on the surface,
  Tinfluence

**Other route: Fundamental Understanding**

**Atomic scale characterization** of the phenomena occurring at the nanoscale at the surface of the sensing layer

- **In situ and advanced characterizations**
- **Theoretical concerns** (DFT calculations)
**Challenge:** Be able to predict and depict phenomena occurring at the surface of sensing layer

- **Provide a predictive simulation of the sensor operation**

**Key points to consider:**
- Molecular level descriptions of atomistic and molecular surface reactions associated charge transfers of each formed surface species

- Understanding of the macroscopic gas sensor behavior as a function of the microscopic aspects of the sensing layer

**Predictive modelling to improve performances facing gas detection**

- **Atomic scale** precision
- **Mesoscopic scale**

**Multi-levels approach**
## Predictive modelling

From atom … to sensor detection

- **Applications**
  
  SnO2 based sensor as a sensing layer
  
  For CO(g) detection

- **Overall methodology**: Multi-levels strategy

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**DFT calculations**

- Adsorbed / formed species
- $\Delta E$ activation barriers
- Kinetics

**Coupled effects**

- **Adsorption**
- **Vacancy**

- **Charge Transfers** $\Delta e$-

- Theoretical IR spectra

And byproducts…

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**2015**
Predictive modelling
From atom ... to sensor detection

- Applications
  SnO2 based sensor as a sensing layer
  For CO(g) detection

- Overall methodology: Multi-levels strategy

I. Atomic Scale insights
  Diving among ‘CO-based’ species existing at the surface of the sensing layer CO(g) and byproducts

II. Toward macroscopic modelling development of the sensor operation

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Atomic Scale Insights

- **Detection of CO(g) on SnO2 surface**

  \[ \Delta E = -0.45 \text{ eV} \]
  \[ \text{CO(ads)} \]

  \[ \Delta E = -0.33 \text{ eV} \]
  \[ \text{CO(formate-like)} + \text{Sn(lat)} \]

  \[ \Delta E = -0.69 \text{ eV} \]
  \[ \text{CO(carboxylate-like)} + \text{O(lat) up or down} \]

  \[ \Delta E = +0.22 \text{ eV} \]
  \[ \text{CO2(g) & V} \]

Byproducts:

\[ \Delta E = 0.16 \text{ eV} \]

\[ E_{ac} = 0.16 \text{ eV} \]
Detection of CO(g) on SnO2 surface

- **Detection of CO(g) on SnO2 surface**

\[ \Delta E = -0.45 \text{ eV} \]

CO(ads)

\[ \Delta E = -0.69 \text{ eV} \]

CO2(ads)

Byproducts:

CO2(g) & V

Eac = 0.16 eV

CT = 0.056

CT = 0.449

CT = 1
Detection of CO(g) on SnO2 surface

\[ \Delta E = -2.62 \text{ eV} \]

CO (carbonate-tridentate-like)

Kinetics to be evaluated ... But seems tricky
- CO(g) on Vacancy as a surface reduction by CO oxidation

Due to kinetics and low adsorption energy: CO(g) diffuses back and forth on the SnO2 surface and adsorbs on Sn(lat) on « perfect lattice »

→ CO2 desorption + V formation favored
**Reaction of CO2(g) as byproduct of CO(g) oxidation – surface reduction**

- \( \Delta E = -0.21 \text{eV} \) for CO2(ads)
- \( \Delta E = -0.15 \text{eV} \) for CO(carbonate-bidentate-like)
- \( \Delta E = -0.36 \text{eV} \) for CO(carboxylate-like)
- \( \Delta E = +1 \text{eV} \) for CO(carbonate-tridentate-like)
- \( E_{ac} = 0.15 \text{eV} \)
- CT = -0.15 eV
- \( \Delta E = -1.32 \text{eV} \)

CT = -0.15
- CO(g) is a reductant gas $\rightarrow$ O depleted surface
- To pursue sensing: An oxygen source is needed

\[ \Delta E = -1.25 \text{ eV} \]

\[ \Delta E = -2.74 \text{ eV} \]
- CO(g) is a reductant gas $\rightarrow$ O depleted surface
- To pursue sensing: An oxygen source is needed

**Catalytic Cycle of reduction / oxidation**

of the SnO$_2$ surface facing CO(g)

1. Oxidation & regeneration
   - SnO$_2$ + O$_2$(ads) + V
2. Reduction
   - SnO$_2$ + V
3. Oxidation
   - SnO$_2$ + O$_2$(ads)
4. Reduction
   - CO

GSSMO, Tübingen - June 8th - 9th, 2015
- Effect of Humidity (1 adsorbed H2O)

\[ \Delta E = -0.4 \text{ eV} \]

\[ \Delta E = -1.42 \text{ eV} \]

\[ \Delta E = -0.34 \text{ eV} \]

\[ \Delta E = 0.047 \]

\[ \Delta E = -1.42 \text{ eV} \]

- CO adsorption in presence of humidity leads to stable structure
- Water is troublesome for CO detection
Summary of DFT results: CO(g) detection on SnO\textsubscript{2}(101) surface

- **CO(g)**
  - CO oxidation $\rightarrow$ Vacancies formation associated to high Charge Transfers $\rightarrow$ O depletion
  - Tricky to form carbonate from CO(g), no carbonyl, no carboxylate
  - Operation under O-environment $\rightarrow$ surface regeneration
    - **a catalytic cycle: oxidation/reduction**

- **CO\textsubscript{2}(g)** (byproduct)
  - Reacts in defects such as Vacancies
  - Form carbonate species

- Carbonates appear as ‘pollutants’ because very stable

- Competition btw O\textsubscript{2}(g) and CO\textsubscript{2}(g) adsorption

- Water decreases CO(g) detection
II. Toward **macrophscopic modelling** development of the sensor operation

- **Applications**
  - SnO₂ based sensor as a sensing layer
  - For CO(g) detection

- **Overall methodology**: Multi-levels strategy

**Software development & simulations**

**Sensor detection**: Gas composition, T, P
Toward a macroscopic modeling from atomic scale considerations

Measure of conductivity
Variations come from electronic transfers caused by reactions (adsorption, products) occurring at the surface of the sensing layer ($\text{SnO}_2$)

- Sensor electric response: controlled by surface chemical reaction
  - Link between Chemistry and ‘electrical response’

SPECIFICATIONS
- $CT$ depend on adsorbed / formed specie on the surface
  - Each specie must be followed
- Depend on concentration of specie
- Depend on kinetics of reaction (rate)
- Depend on Temperature and pressure operation

Macroscopic code developed under atomic scale considerations
→ Mixing all DFT events / Interplay of the different reactions
Toward a macroscopic modeling from atomic scale considerations

- **Kinetic Rates Theory**

  \[ A + B \leftrightarrow C \]

  \[
  \frac{-d[A]}{dt} = \frac{-d[B]}{dt} = \frac{d[C]}{dt} = k_i \cdot [A] \cdot [B] - k_{-i} \cdot [C]
  \]

  - Rate constants are kinetics of the reactions (DFT activation barrier)

  \[
  k_i = \frac{k_B T}{h} \times \exp\left(\frac{-\Delta E_i}{k_B T}\right)
  \]

- **CTα Specie concentration**

  \[
  \frac{d(CT)}{dt} = \sum_i CT_i \frac{d[i]}{dt}
  \]

- **Detection Operation**

  Gas Flux: Maxwell-Boltzmann Statistics

  \[
  C \frac{P_{gas} S}{\sqrt{M_{gas} T_{gas}}}
  \]
Toward a macroscopic modeling from atomic scale considerations

Illustrations: Chemical kinetics for CO(ads) species & 2 surface reactions

- **Physisorption**: Weak interaction, physisorption
- **Chemisorption**: Strong interaction, covalent link

To do for each species on the surface (CO(ads), carb, CO2(ads), Sn(lat), O(lat), V...) for all reactions
Toward a macroscopic modeling from atomic scale considerations

- Signal varies with the Concentration
- No significant signal for CO(g) detection

$T_{\text{gas}} = 300 \, \text{K}$

$600 \, \text{K}$

- 1 ppm
- 200,000 ppm
- 200 ppm

- No significant signal for CO(g) detection
Toward a macroscopic modeling from atomic scale considerations
Conclusions

- **DFT**
  - A non exhaustive list of surface chemical reactions
  - Catalytic oxidation mechanism of CO involving successive reduction and reoxidation of the oxide layer
  - CO detection:
    - characterization of SnO₂-catalyzed CO combustion
    - SnO₂ reoxidation step being slower: accumulation of vacancies → negative charge transfer // conductivity increases
    - fast and highly exothermic reactions, large charge transfers → easy detection
  - CO₂ detection:
    - CO₂ form stable carbonate specie
    - small charge transfers → small electric response per CO₂ → troublesome detection
  - Sensitivity to interferents (H₂O)

- **Mesoscopic modelling**
  - CO detection by the sensor
  - CO₂ detection is troublesome due to weak response
  - Interfering role of H₂O
Conclusions

- Agreement with the experimental surface characterizations and with experimental tendencies on conductivity measurement
  - Increase of the sensor conductivity under CO(g) exposure
  - Uneasy CO₂(g) detection
  - Interfering role of H₂O

- Multi-levels modeling to support technological development of sensor

- To provide tool for engineer and propose new routes toward nano-engineered materials

- Water role & Thermodynamics (T, P, vibrational properties) must be fully understand to consider interplay of external parameters → our future modeling goal