Semiconductor gas sensors

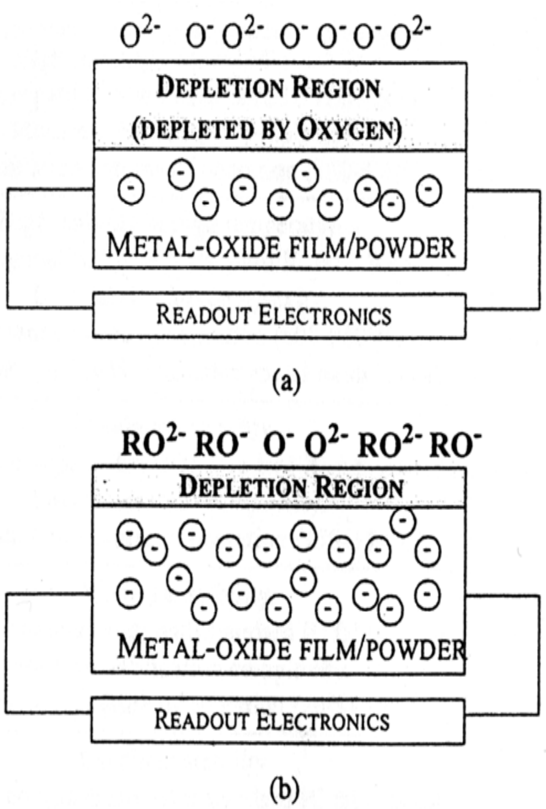
Outline

- Introduction: Chemiresistors, general operation and limitations
- Chemical imaging: Kelvin probe method
- Epitaxial tin dioxide films

Semiconductor gas sensor

- SnO2 based sensor (chemiresistors) are predominant solid-state gas sensors for domestic, commercial and industrial application.
- Low cost
- Easy production
- Rigid construction
- Compact size
- Simple measuring electronics

Metal-oxide semiconductor chemical microsensor



- Oxygen extract electrons from metal-oxide film thereby decreasing conductivity
- When reducing agent is present, electrons are injected into the material and increasing conductivity

The main limitations for chemiresistors: low selectivity and stability

-Chemiresistors are broadly selective, responding to large family of chemicals, such as all reducing gases.

-Chemiresistors exhibit high noise and long term instability due to polycrystalline nature of the sensing film with response related to grain boundaries and surface interactions.

-Batch reproducibility of the sensing film is highly variable due to random variation in the film surface that occur during fabrication process

"Hot Electron"

The ways for overcoming the selectivity problem

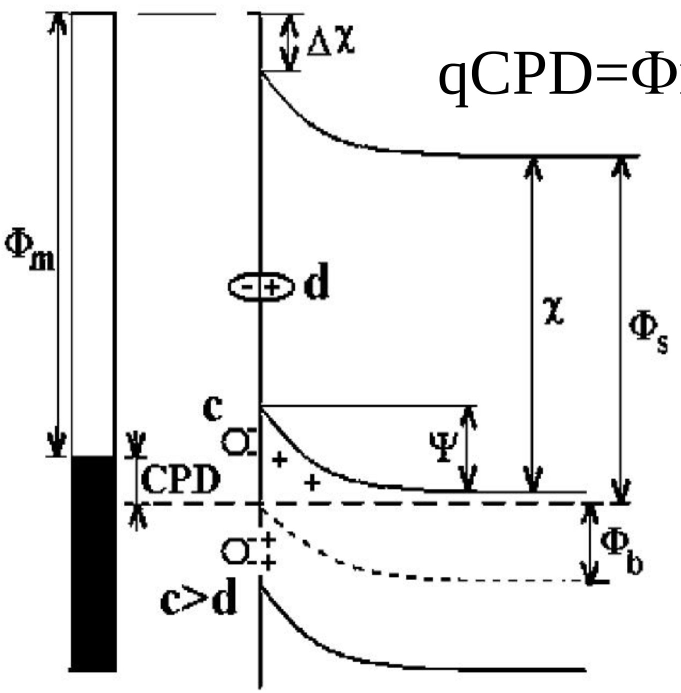
- Additional of catalysts
- External filters
- Adjustment of operation parameters such as temperature
- Sensor array with data analysis.

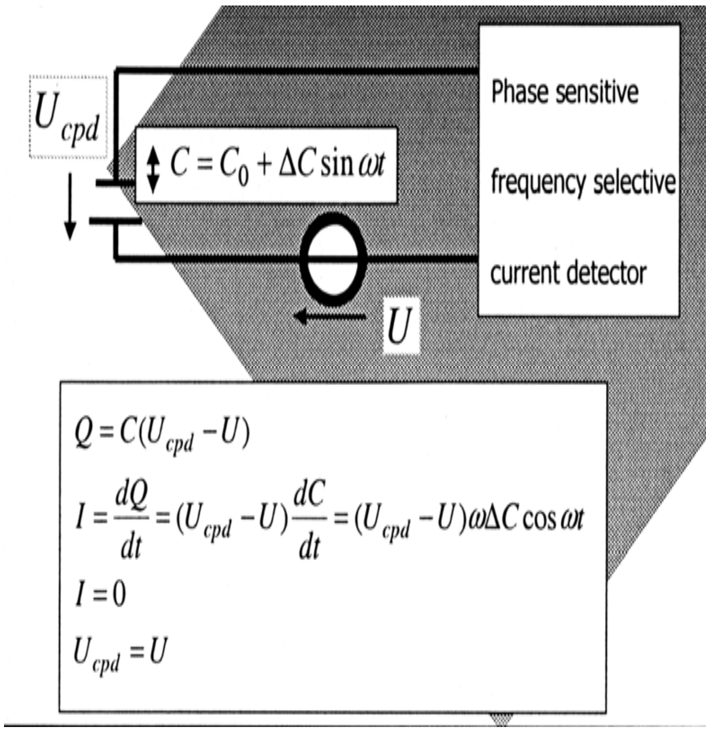
Chemical imaging

- Chemical image can be composed from the output signals of a multi-sensor system
- Different materials can be deposited on a wafer and response can be read by scanner
- Temperature or/and concentration gradient can be arrange along sample surface and response can be read by scanner

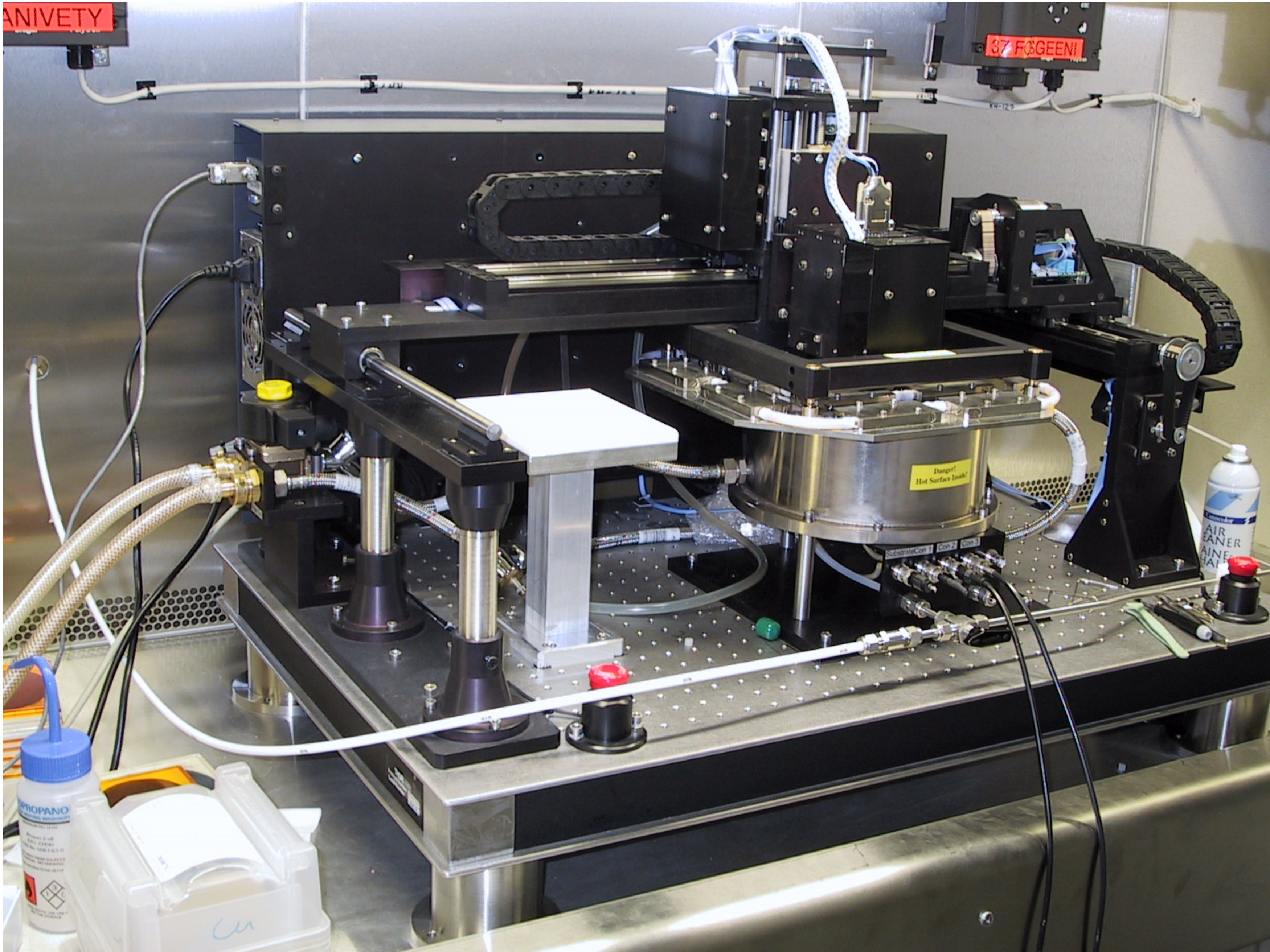
Band diagram and schematic illustration of the surface potential measurement setup

$$qCPD=\Phi m-\Phi s-q\psi-\Delta\chi$$

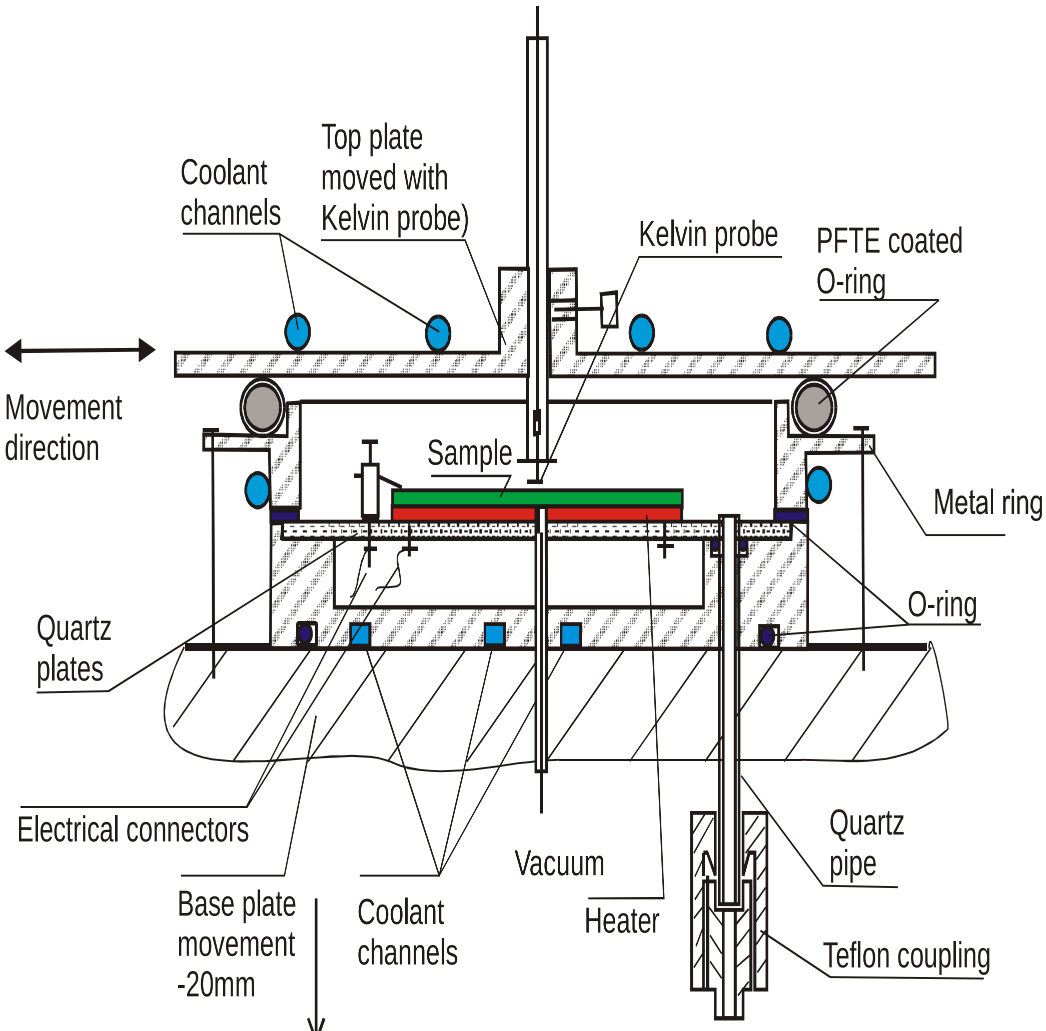




Vibrating capacitor method is sensitive for contact potential difference (CPD) between a vibrating reference electrode and the surface to be investigated.

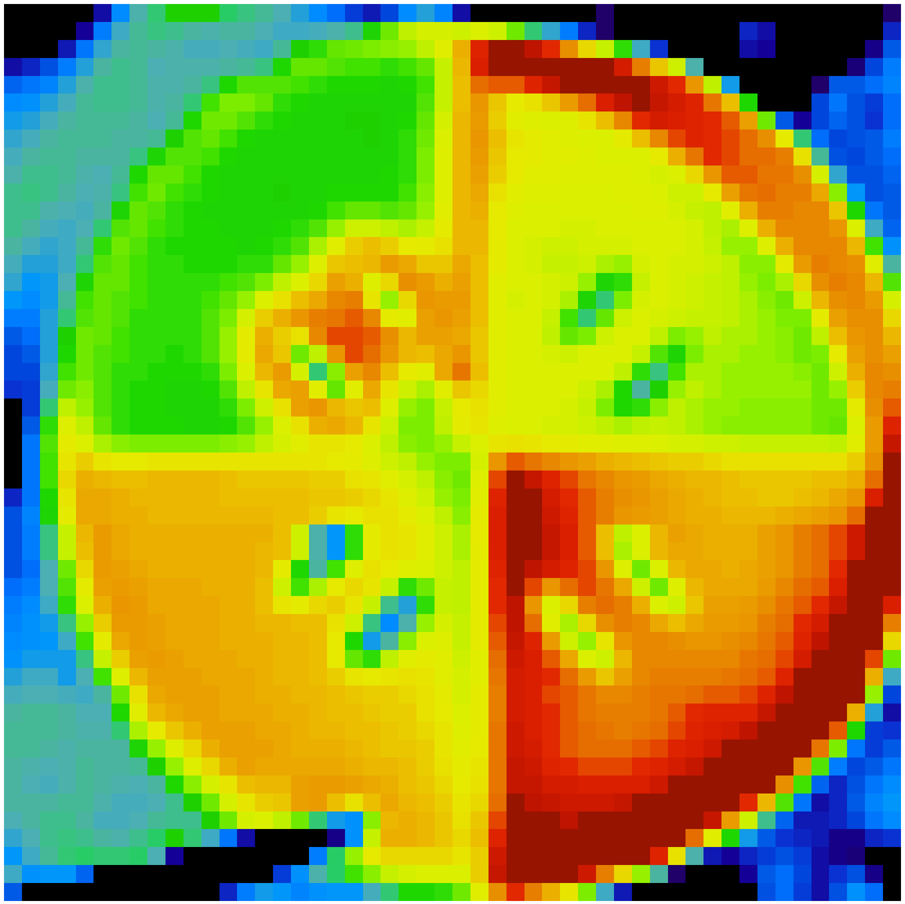

Danger!
Hot Surface Inside!
SubstrateCon 1
Con 2
Con 3

Schematic cross-section of the Kelvin measuring chamber



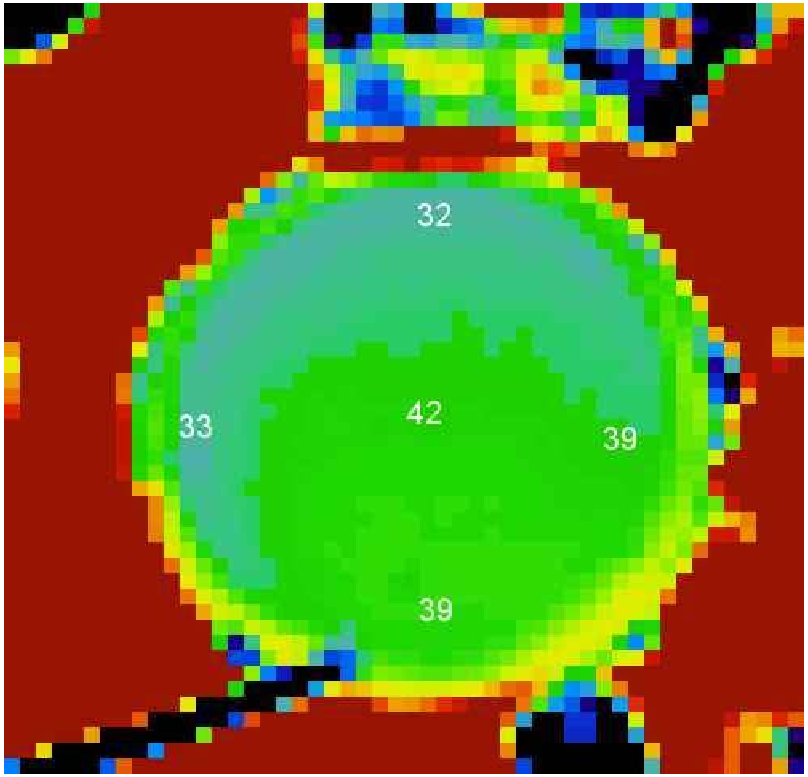
- Sample is placed into closed chamber with controllable gas atmosphere
- Sample temperature is in range of 20-400C.
- Chemical image is acquired by scanning vibration capacitor.
- Lateral resolution is 2mm

Kelvin potential map of the 4-segments sample with different catalyst layers



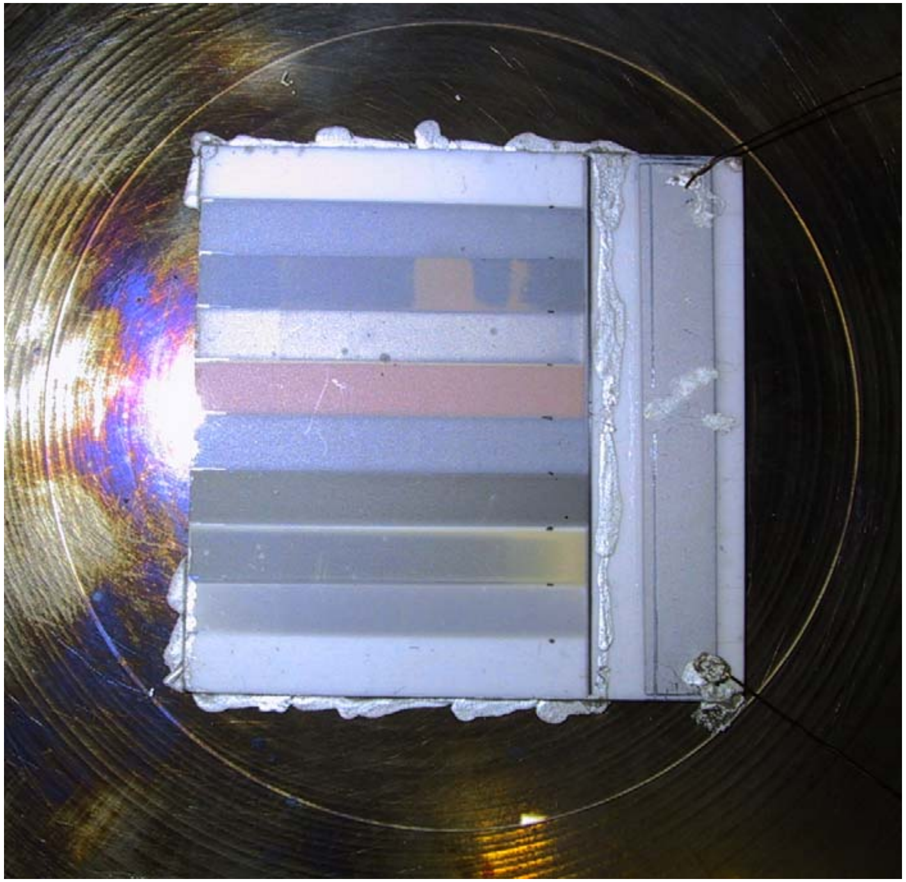
- 100 nm SnO_2 layer on $Si/SiO_2/Si_3N_4/Ta_2O_5$ substrate.
- 5nm Pt, Pd and Ni were deposited by E-beam evaporation.
- 100nm Au contacts were deposited for resistivity measurement

Correlation between surface resistivity and potential distribution



- 100nm SnO_2 made by reactive E-beam deposition in MBE
- Sheet resistance was measured by 4-probe method.
- Uniform color tone corresponds more uniform potential distribution

“Two dimensional” chemical imaging.

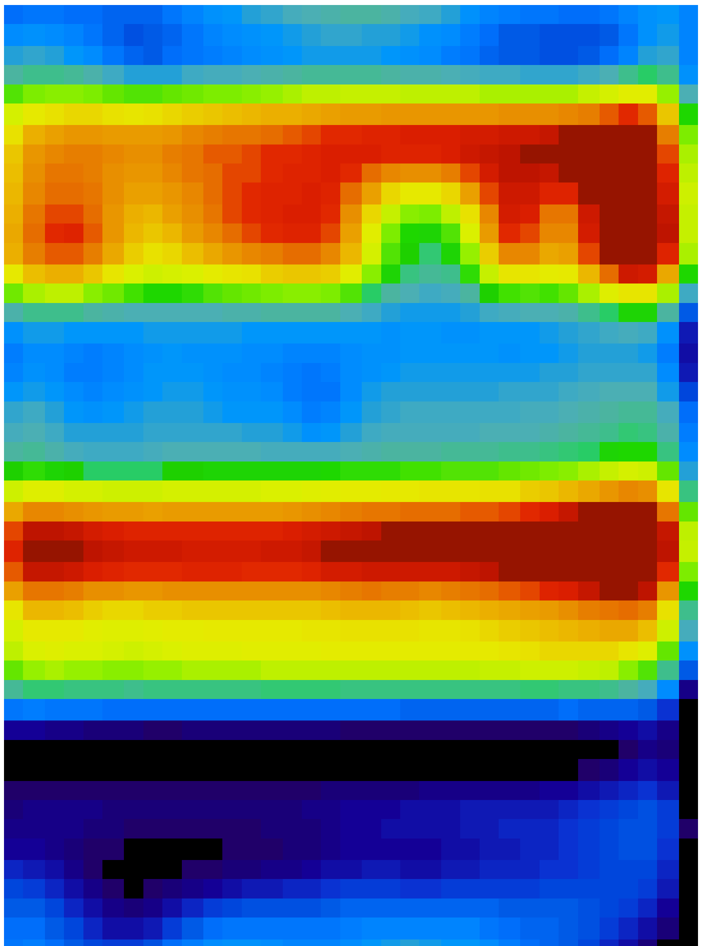


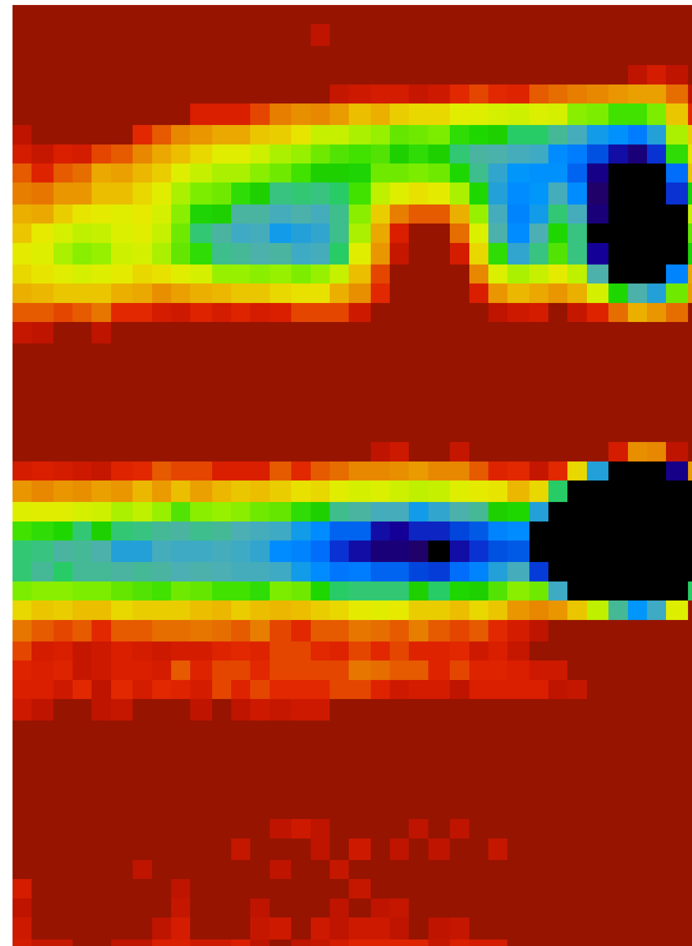
-SnO_2-Pd-PdO-Ag-Au-Pt-V-Cu-W-SnO_2 strips sputtered on ceramic substrate.

-Silica disk is using for thermal insulation.

-Pt heater provides the thermal gradient about 50C along x axis.

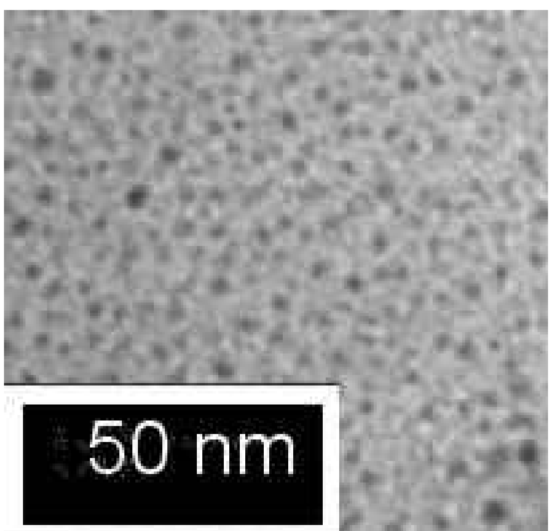
Kelvin potential map and response to 100ppm of alcohol for the sample with the different catalyst strips and temperature gradient





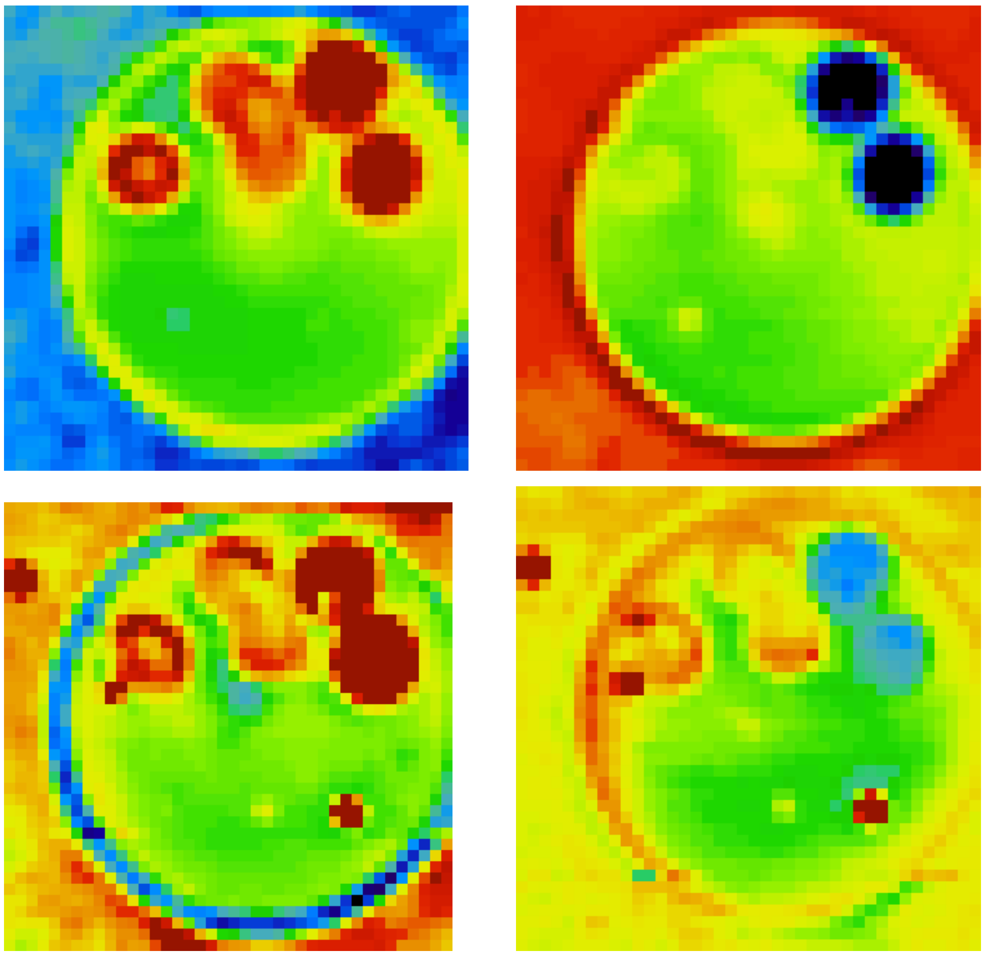
"Hot Electron"

Catalyst nanocrystal synthesis.



- Nature Vol 437 p121-124
- Liquid-solid-solution phase transfer synthesis.
- Final products – noble metal nanocrystals 1-10nm size dispersed as colloidal solution in organic solvent.
- Nanocrystals can be put to the surface by dropping the colloidal solution and solvent drying.

Kelvin gas response for SnO2 modified by different catalysts.

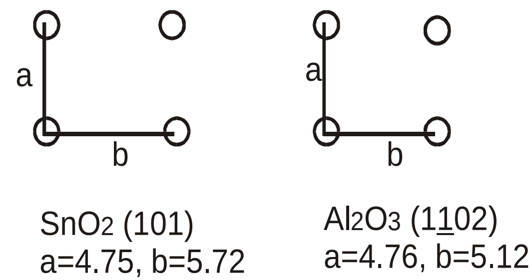


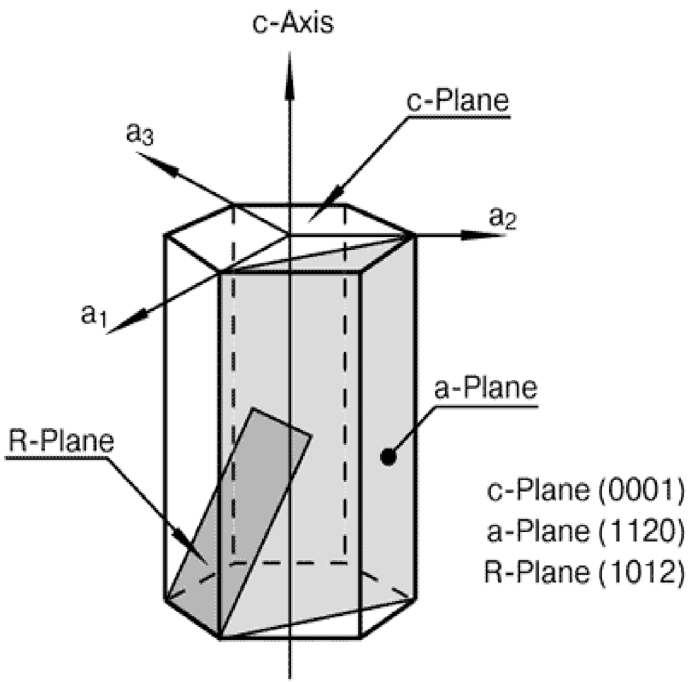
-SnO2 layer modified by Pt nanocrystals (left, center) Pt+Ru (right-top), Ru (right)
- Kelvin map (top left) and gas response for 100ppm of alcohol (top right), HCN (bottom left) and COCl2 (bottom right).

Epitaxial tin dioxide films

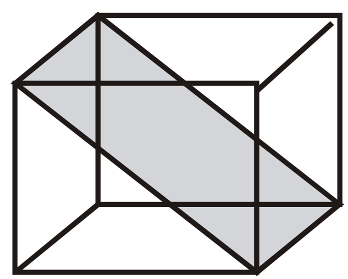
- Reliability and reproducibility is dependant on signal drift over time.
- Properties of SnO_2 films strongly depend on the microstructure.
- Presents of grain boundaries gives complex responses due to electron trap states formed at the interfaces.
- Fast response, good reliability expected for epitaxial sensing films.

Crystal structures of sapphire and tin dioxide





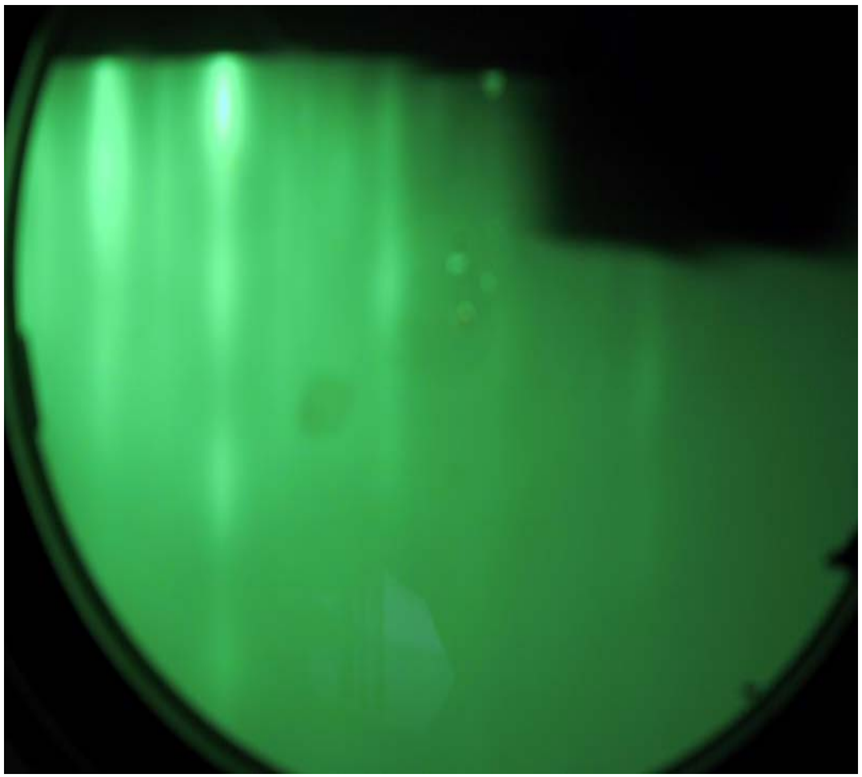
Hexagonal



Tetragonal

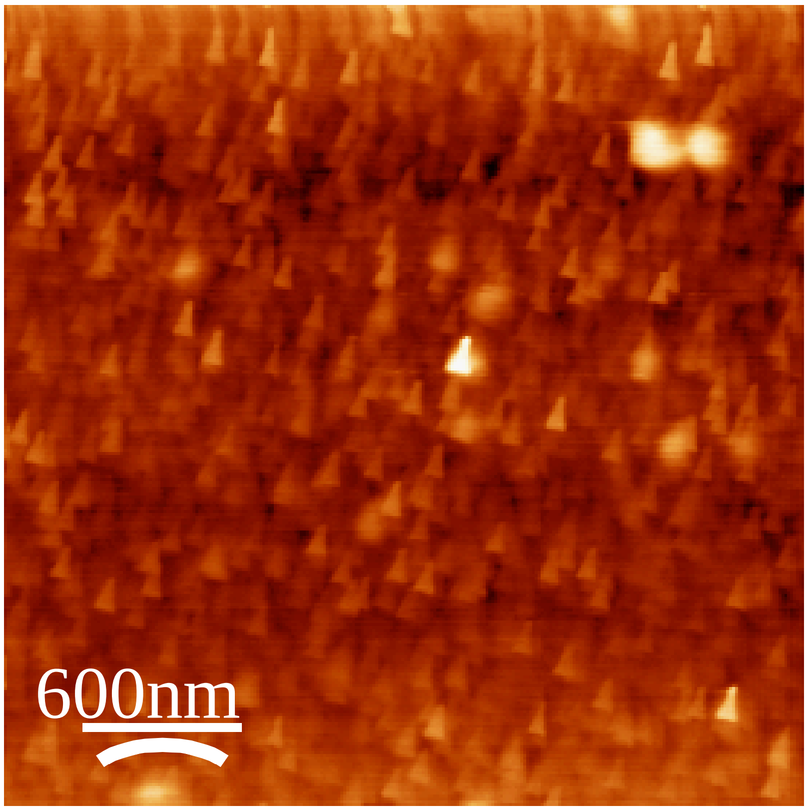
- Crystal structures are different
- Sapphire R-plane has small misfit with SnO_2 (101) plane

High energy electron diffraction image from as-gown SnO2 film



- Reactive deposition of Sn with rate 0.02nm/s under oxygen pressure 1e-5 bar. Substrate temperature was 600C.
- RHEED pattern like modulated lines corresponds highly oriented film with moderate surface roughness.

AFM image of as-grown SnO_2 film



- Pyramid-like structures are observed on sample surface
- Thin film has separate SnO_2 islands (no surface conductivity)
- Islands merging leads to high defect density

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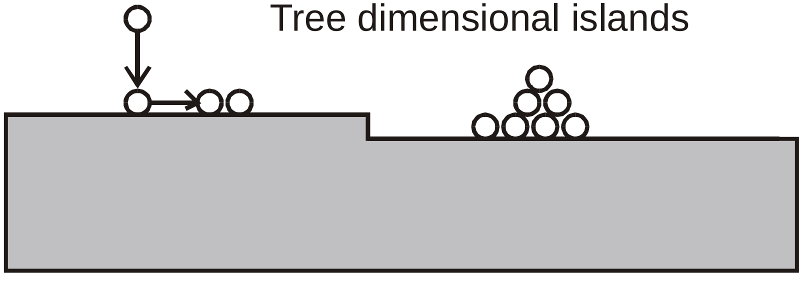
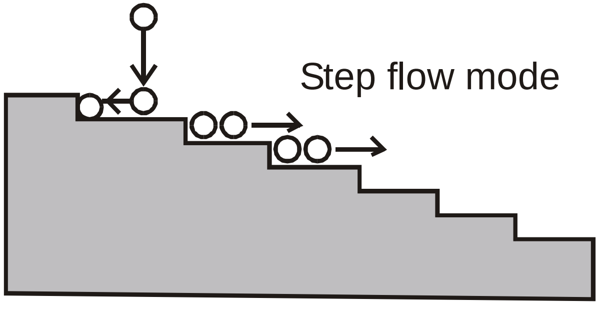
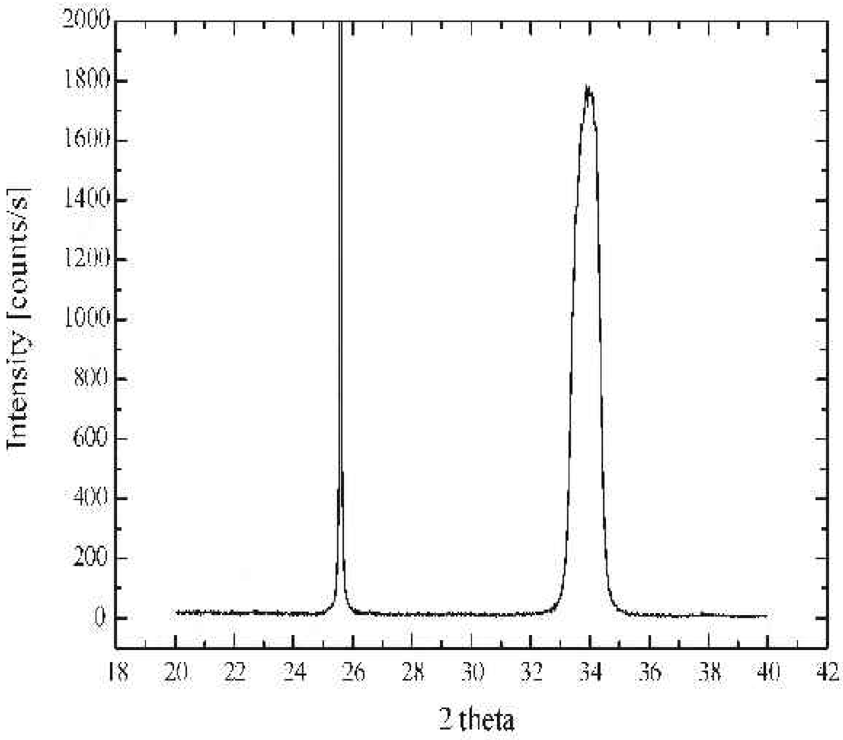
SnO_2/Al_2O_3 growth model





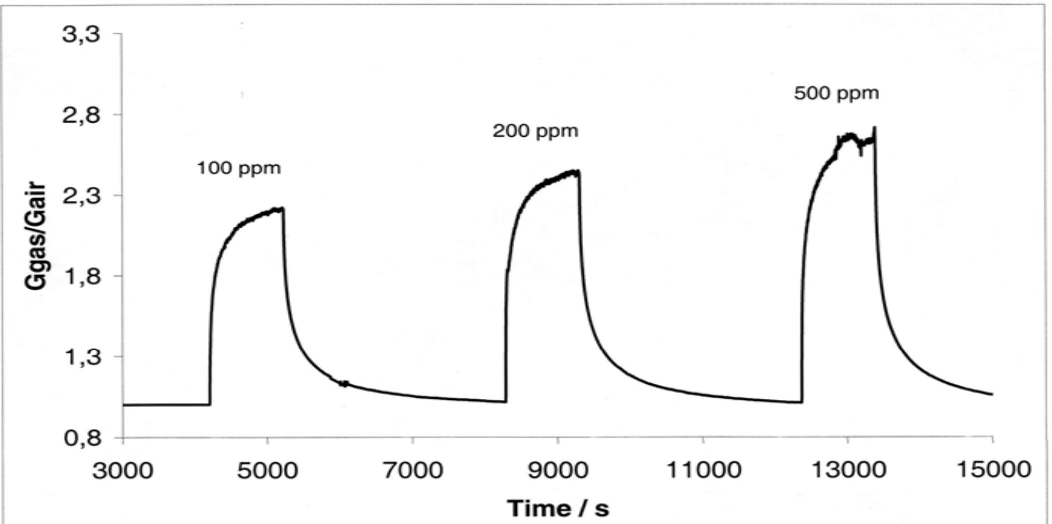
- Substrate with exact orientation has large terraces without steps
- Due to large surface energy of SnO_2 (101) plane is 3-dimensional growth mode
- Step flow growth mode expected for missoriented substrate

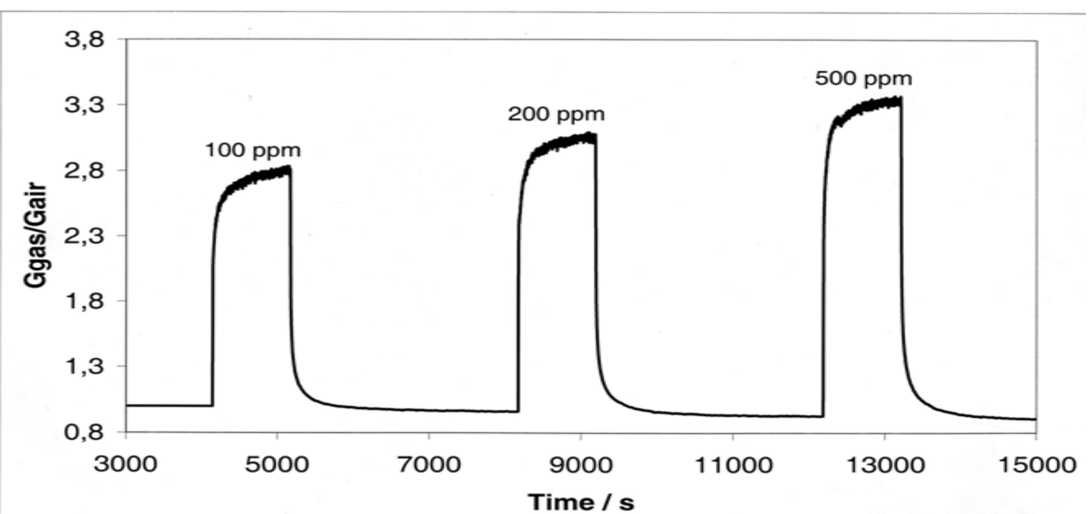
XRD Θ–2Θ curve for 100nm SnO_2 on sapphire.



- Unique (101) SnO_2 diffraction peak indicates that SnO_2 film is highly oriented along the substrate.
- Large width of (101) SnO_2 diffraction peak corresponds large amount of defects in the film.

Response for ethanol for polycrystalline (top) and highly oriented (bottom) SnO2 films.





-Polycrystalline film was deposited with the similar growth parameters at low temperature.

-Polycrystalline film has significantly longer rise and decay times.