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
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 arranged along sample surface and response can be read by scanner.
Band diagram and schematic illustration of the surface potential measurement setup

\[ q\text{CPD} = \Phi_m - \Phi_s - q\psi - \Delta \chi \]

Vibrating capacitor method is sensitive for contact potential difference (CPD) between a vibrating reference electrode and the surface to be investigated.
Schematic cross-section of the Kelvin measuring chamber

- Sample is placed into closed chamber with controllable gas atmosphere
- Sample temperature is in range of 20-400°C.
- 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 SnO2 layer on Si/SiO2/Si3N4/Ta2O5 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 SnO2 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.

-SnO2-Pd-PdO-Ag-Au-Pt-V-Cu-W-SnO2 strips sputtered on ceramic substrate.
-Silica disk is using for thermal insulation.
-Pt heater provides the thermal gradient about 50°C along x axis.
Kelvin potential map and response to 100ppm of alcohol for the sample with the different catalyst strips and temperature gradient.
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 SnO2 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

- Crystal structures are different
- Sapphire R-plane has small misfit with SnO$_2$ (101) plane

SnO$_2$ (101)  
$a=4.75$, $b=5.72$

Al$_2$O$_3$ (1102)  
$a=4.76$, $b=5.12$

Hexagonal  
Tetragonal
High energy electron diffraction image from as-grown SnO2 film

- Reactive deposition of Sn with rate 0.02nm/s under oxygen pressure 1e-5 bar. Substrate temperature was 600°C.
- RHEED pattern like modulated lines corresponds highly oriented film with moderate surface roughness.
AFM image of as-grown SnO\textsubscript{2} film

- Pyramid-like structures are observed on sample surface
- Thin film has separate SnO\textsubscript{2} islands (no surface conductivity)
- Islands merging leads to high defect density
SnO2/Al2O3 growth model

- Substrate with exact orientation has large terraces without steps
- Due to large surface energy of SnO2 (101) plane is 3-dimensional growth mode
- Step flow growth mode expected for missoriented substrate
XRD $\Theta$–$2\Theta$ 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.