

Sputter-deposited Nanostructured Metal-Oxide Films for Hydrogen Gas Sensing

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Hydrogen Gas Sensor

Motivation

Expansion of hydrogen-based technologies demands more advanced measurement and control of hydrogen concentrations. This brings **new challenges** for material researchers working in the field of **gas sensors**.

Metal oxides are well established as active materials in gas-sensor assemblies. Often they are used in **conductometric** sensors where the conductivity of a sensor in dependency on the concentration of the monitored gas is studied.

The sensorial response can be enhanced by **combining of proper materials** and/or by changing geometrical properties of sensor assembly (e.g., **enlarging of active surface area**).

Thin Film + Nanoclusters

WO₃

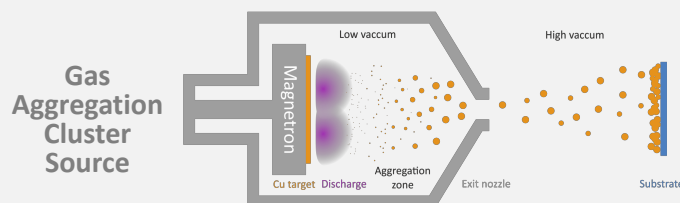
CuO

Thin layers of WO₃ deposited by **Reactive Magnetron Sputtering**

- DC magnetron
- W metal target
- Ar + O₂ working gas
- substrate at 500 °C

Clusters sputter deposited in **Magnetron-based Gas Aggregation Cluster Source**

- Cu metal target
- Ar working gas
- various densities prepared

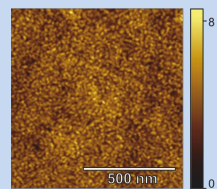
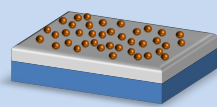


Thin film WO₃

Investigated Specimens

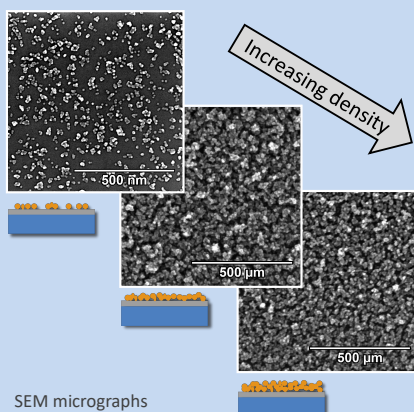
+ Clusters Cu

Increasing density

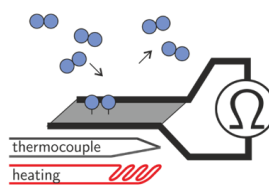


AFM topography of WO₃ surface (no clusters)

SEM micrographs

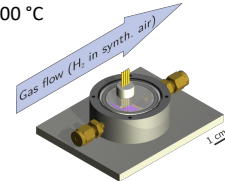


Conductometric Gas Sensor



Gas Flow Reactor

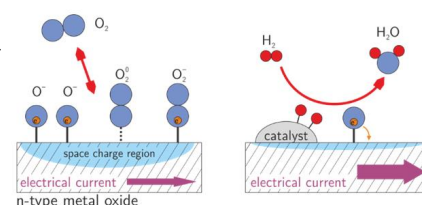
- 4PP resistance measuring
- 300 °C



Sensing mechanism

depicted for *n*-type semiconductor

- preadsorbed O₂ gathers free electrons
- dissociation of H₂ often assisted by noble metal
- reaction of H and O species returns electron to the SC



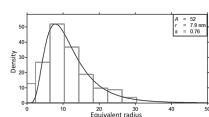
Film Properties

- thickness (AFM) 30 nm
- stoichiometry (EDS, XPS) WO₃
- crystallinity (XRD) orthorhombic

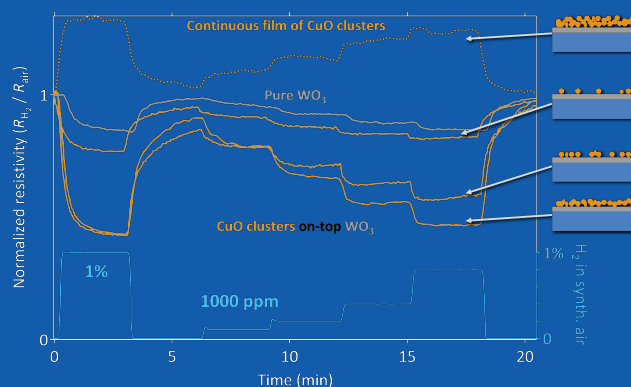
Cluster Properties

- stoichiometry (XPS) CuO

- size (SEM, AFM) diameter ~ 10 nm

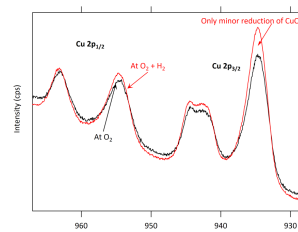


Response of System to Hydrogen Gas



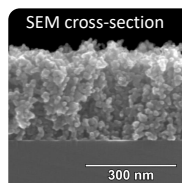
- Enhanced sensitivity with CuO clusters
- Opposite reaction of continuous film of CuO clusters contrary to WO₃ thin film

Near Ambient Pressure Photoemission Spectroscopy



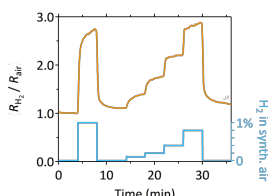
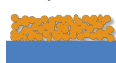
- 300 Pa O₂, 300 °C, + 30 Pa H₂
- copper in a form of cupric oxide (CuO)
- remains oxidic during and after the exposition to H₂
- WO₃ stable

SEM cross-section



Nanocluster Sensor

- this time just CuO clusters
- extremely high surface active area
- high sensitivity



Explanation

- Copper does not play a role as a catalyst.
- WO₃ is *n*-type semiconductor × CuO is *p*-type semiconductor → opposite response
- *p-n* junction is formed reacts with preadsorbed O₂ and H₂ → enhanced response

