

ALD H₂-sensor for in-sensor computing crossbar array

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M-ERA.NET project ATOSENS = Atomic-layer 3D printing as a new paradigm for smart sensorics

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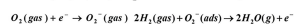
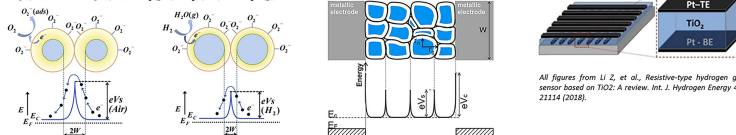
ATLANT
3D NANOSYSTEMS

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H₂ sensing mechanism in TiO₂

Obtaining high quality TiO₂ thin films with nanocrystalline morphology resulting in dense grain-boundary network is essential for high sensitivity towards H₂.

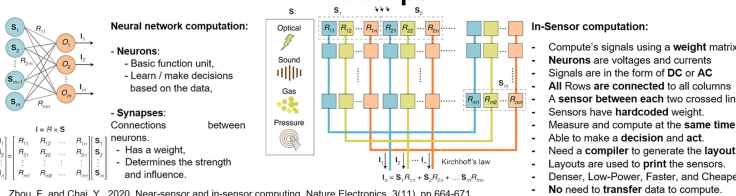


a) The illustration of general hydrogen sensing mechanism (ionosorption model) of TiO₂ based sensors for layers with grain boundaries. Oxygen adsorbed on grain boundaries captures free electrons from the conduction band which results in increased resistance. Hydrogen exposure leads to a reaction with ionized oxygen releasing the captured electrons hence decreasing the resistance of TiO₂.

b) Sketch of the conduction band profile. Here E_c is the flat band energy, eV_g is the Schottky barrier, eV_g is the intergrain energy barrier due to the electron depletion, r_g is the grain radius, and m is the radius of the neutral (undepleted) grain region. For good sensing, it is desired to $r_g \ll r_g$ and $eV_g \ll eV_g$.

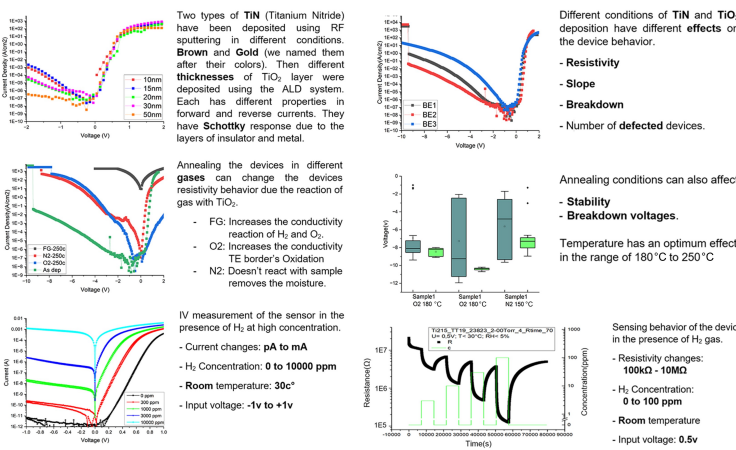
c) Sandwich-type TiO₂ thin-film H₂ gas sensor. The top electrode/TiO₂ interface is the most sensitive region for hydrogen sensing.

Concept

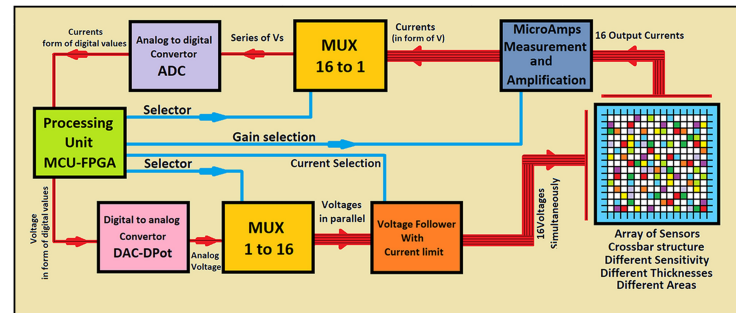
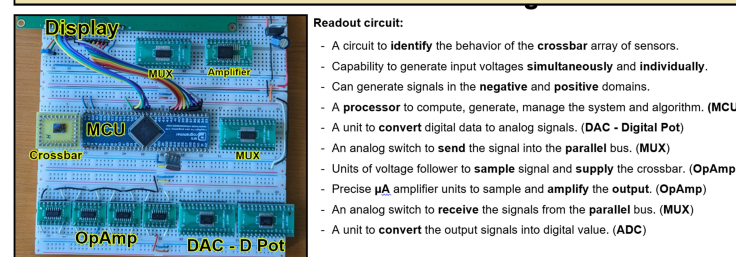


Zhou, F. and Chai, Y., 2020. Near-sensor and in-sensor computing. Nature Electronics, 3(11), pp.664-671.

Characterization



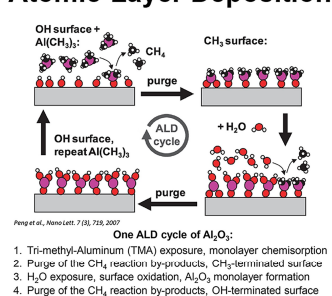
Readout circuit



Readout circuit:

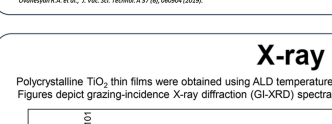
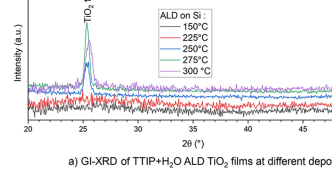
- A circuit to **identify** the behavior of the **crossbar** array of sensors.
- Capability to generate input voltages **simultaneously** and **individually**.
- Can generate signals in the **negative** and **positive** domains.
- A **processor** to compute, generate, manage the system and algorithm. (**MCU**)
- A unit to **convert** digital data to analog signals. (**DAC - Digital Pot**)
- An analog switch to **send** the signal into the **parallel** bus. (**MUX**)
- Units of voltage follower to **sample** signal and **supply** the crossbar. (**OpAmp**)
- Precise **µA** amplifier units to **sample** and **amplify** the output. (**OpAmp**)
- An analog switch to **receive** the signals from the **parallel** bus. (**MUX**)
- A unit to **convert** the output signals into digital value. (**ADC**)

Atomic-Layer Deposition



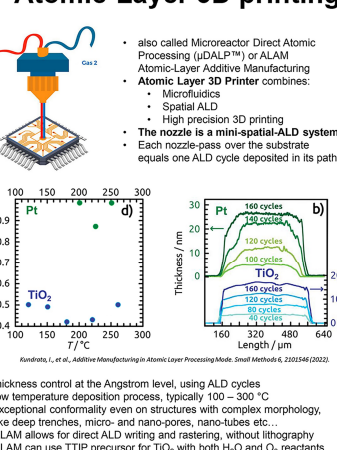
One ALD cycle of Al₂O₃:

1. Tri-methyl-Aluminum (TMA) exposure, monolayer chemisorption
2. Purge of the CH₃ reaction by-products, CH₃-terminated surface
3. H₂O exposure, surface oxidation, Al₂O₃ monolayer formation
4. Purge of the CH₃ reaction by-products, OH-terminated surface



a) GI-XRD of TTIP+H₂O ALD TiO₂ films at different deposition temperatures on a) Si substrates, b) 30 nm Pt-on-Si substrates.

Atomic-Layer 3D printing

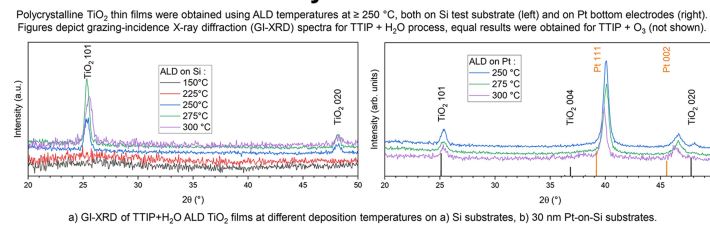


also called Microreactor Direct Atomic Processing (µDALP™) or ALAM

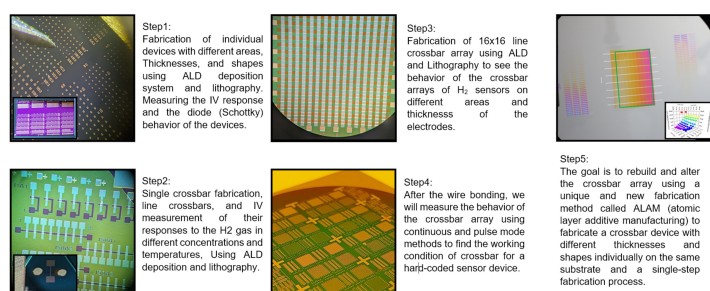
- Atomic-Layer Additive Manufacturing
- Atomic-Layer 3D Printer combines:
 - Microfluidics
 - Spatial ALD
 - High precision 3D printing
- The nozzle is a mini-spatial-ALD system
- Each nozzle-pass over the substrate equals one ALD cycle deposited in its path

- thickness control at the Angstrom level, using ALD cycles
- low temperature deposition process, typically 100 – 300 °C
- exceptional conformality even on structures with complex morphology, like deep trenches, micro- and nano-pores, nano-tubes etc...
- ALAM allows for direct ALD writing and rastering, without lithography
- ALAM can use TTIP precursor for TiO₂ with both H₂O and O₃ reactants

X-ray diffraction



Fabrication Method



Summary & Key points

- The goal of this work was to study whether thin TiO₂ films deposited by ALD can be used for hydrogen sensors. with the aim to utilize atomic-layer 3D printing (ALAM) for the fabrication of these sensors in the next phase of the ATOSENS project.
- For high sensitivity towards H₂ gas, TiO₂ thin film with a nanocrystalline morphology and dense grain-boundary network is required.
- Physical properties such as thickness and area can change the behavior or sensing device and by using these factors, different crossbar arrays have been fabricated using the common methods. (Lithography, ALD, PVD)
- Electrical measurement shows that TiO₂ deposition conditions, Top and bottom electrode material, and annealing conditions have a great impact on the behavior of the devices.
- Response ((R_{air}-R_{H2})/R_{H2}) of ~10³ was recorded at room temperature for 20 nm thick ALD films made using TTIP and H₂O.
- By finding the right area, thickness, and position of each device in the crossbar array using simulation, a desirable layout capable of measuring and computing can be generated.
- Using the Atomic Layer 3D printer, there is a possibility to fabricate the generated layout with different thicknesses, areas, and deposition conditions on a crossbar array chip in a single run without the need for lithography masks, deposition, and etching.

Acknowledgment

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