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Hydrogen gas sensing performance of high-dimensional tungsten oxide fuzz(He induced nanostructure)

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Background

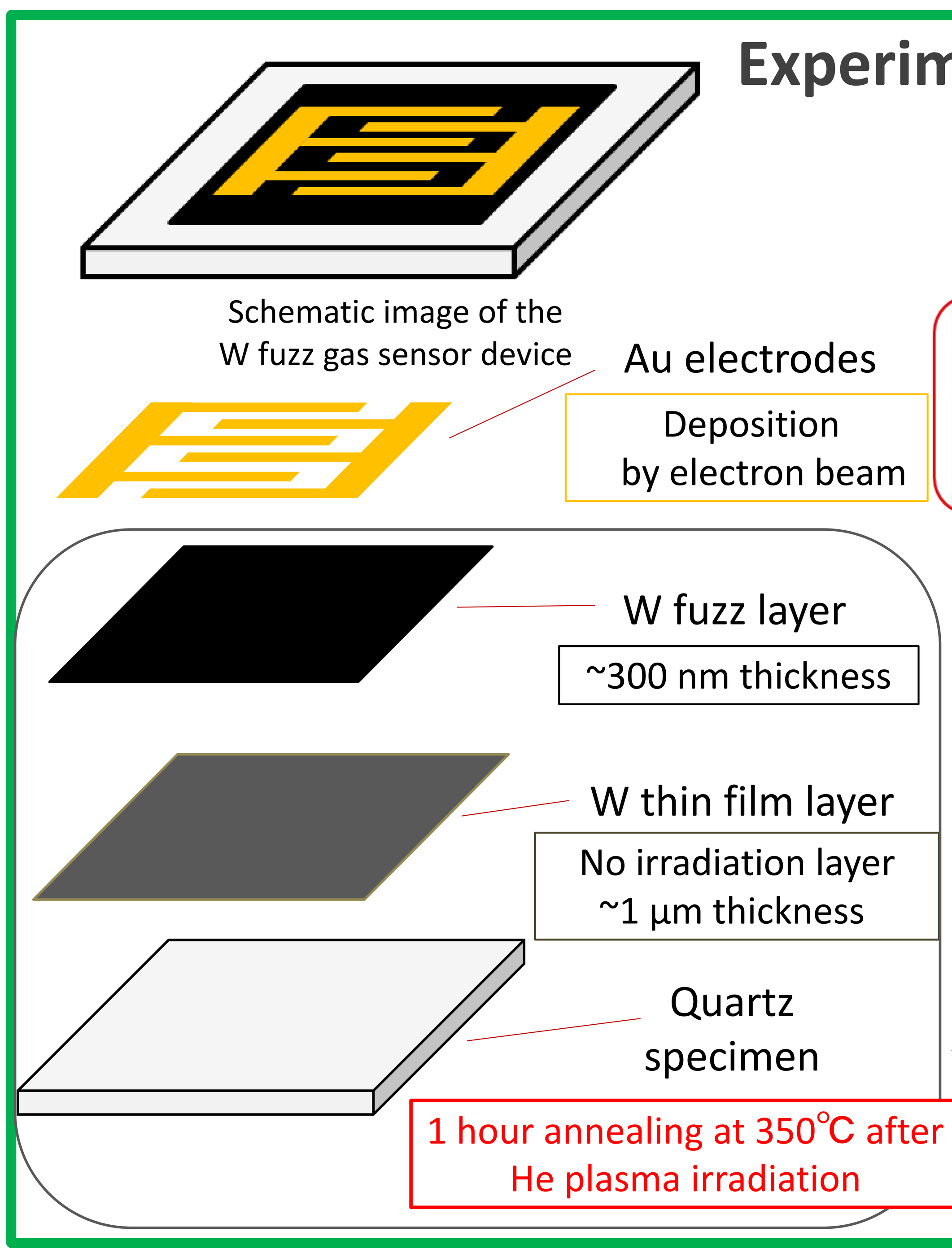
- Characteristic nano-structures are formed by He plasma irradiation of metals at certain temperatures.
- This nano-structure, called '**fuzz**', is expected to be applied to catalysts and sensors because of their remarkably large surface area due to high-dimensionality.
- Tungsten oxide exhibits promising hydrogen sensing properties through redox reaction.
- Demand for hydrogen sensor is high with hydrogen fuel etc., concentration detection at 10ppb level is necessary.
- Performance improvement by fuzz nanostructure in gas sensor is confirmed in ethanol(ppm) sensing in our previous study[1].

[1] K. Ibano *et al.*, J. Appl. Phys. 57(2018)040316.

Purpose

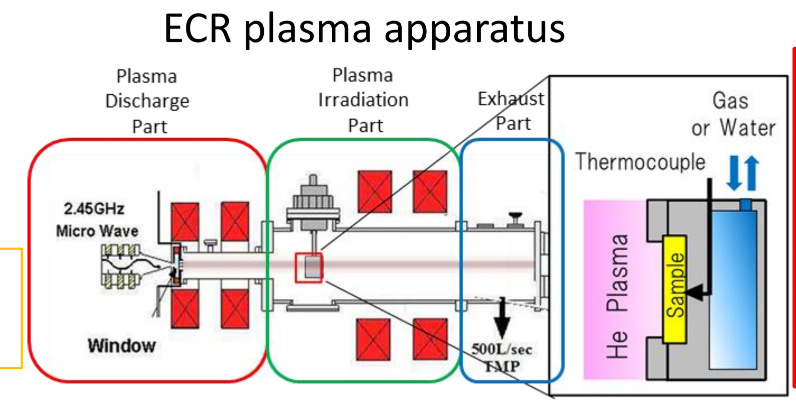
- To develop **high performance hydrogen gas sensor** using tungsten oxide fuzz(He induced nanostructure) with high sensitively.

Experiments



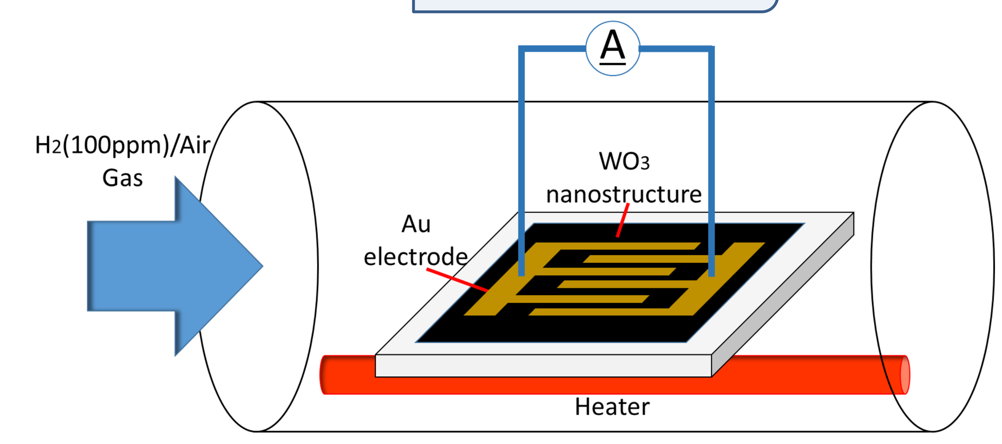
Fuzz Nanostructure Formation

ECR plasma apparatus



<Conditions>
Plasma Parameters
- Flux: 1×10^{22} m^{-2}s^{-1}
- Fluence: 1.8×10^{26} m^{-2}
- Gas: He (50mTorr)
- Temperature: 900K
- Vias voltage : 200V

Gas Sensing



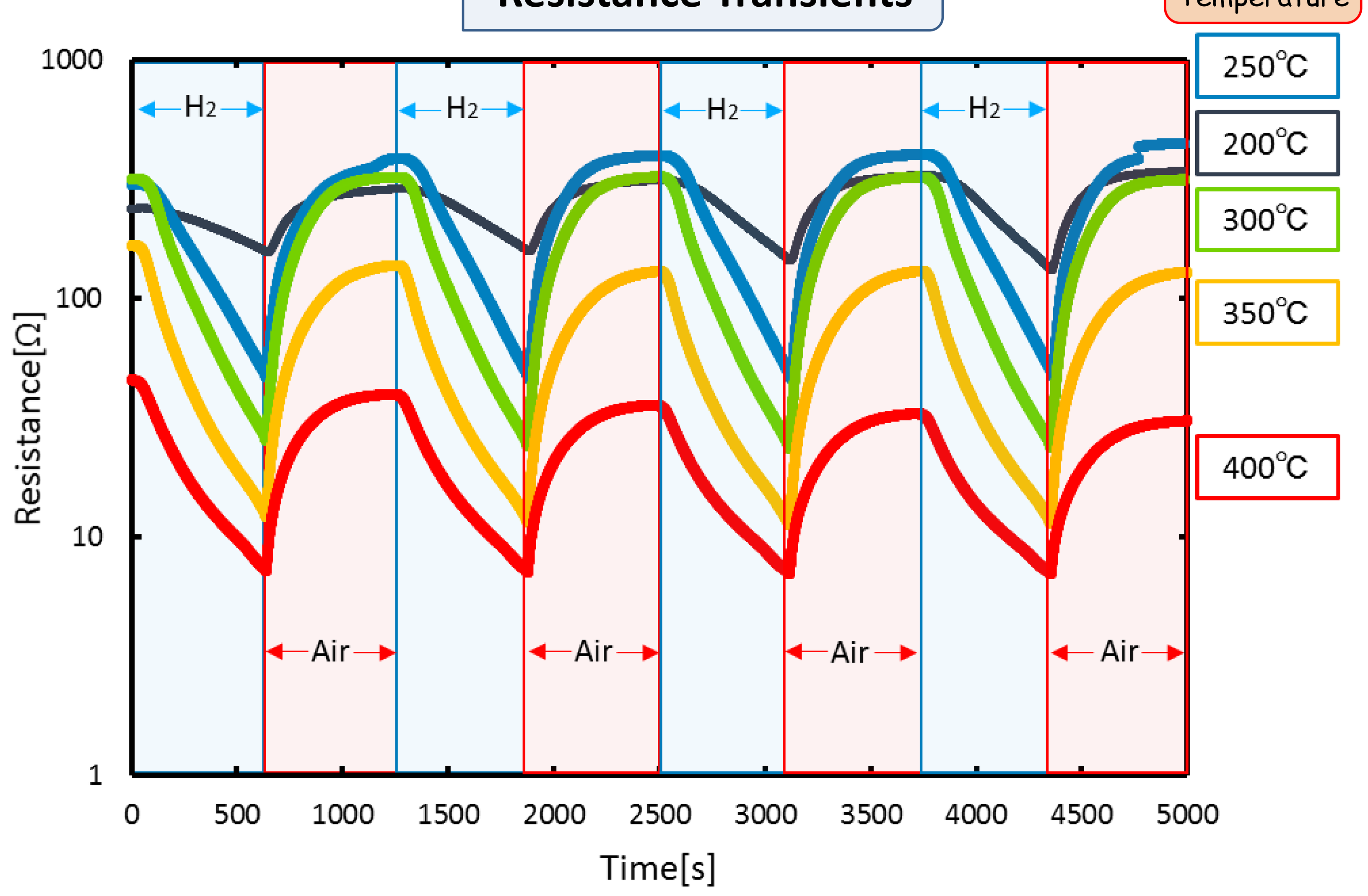
- Sensing test was carried out by placing the sample in a glass tube, switching between H_2 gas (100 ppm,the rest is N_2) and dry air (O_2:22%, N_2:78%) while heating with IR heater and measuring the electrical resistance.

Conclusion

- By using W fuzz, hydrogen gas sensors was developed. Change in the electric resistance during H_2 flow were improved with a higher resistivity during air flow (R_{Air}). For 100 ppm H_2 flow, the change was 1 order of magnitude when R_{Air} is several hundreds of ohms and the change was 2 order of magnitude when R_{Air} is several mega ohms.
- R_{Air} varies greatly depending on oxidation temperature, and both W fuzz sensors showed the largest change when the operating temperature was 300°C.
- W fuzz oxidized at 450°C showed the reactivity of **99.5%** suggesting higher reactivity could be obtained by oxidizing at higher temperatures.

Result & Discussion

Resistance Transients

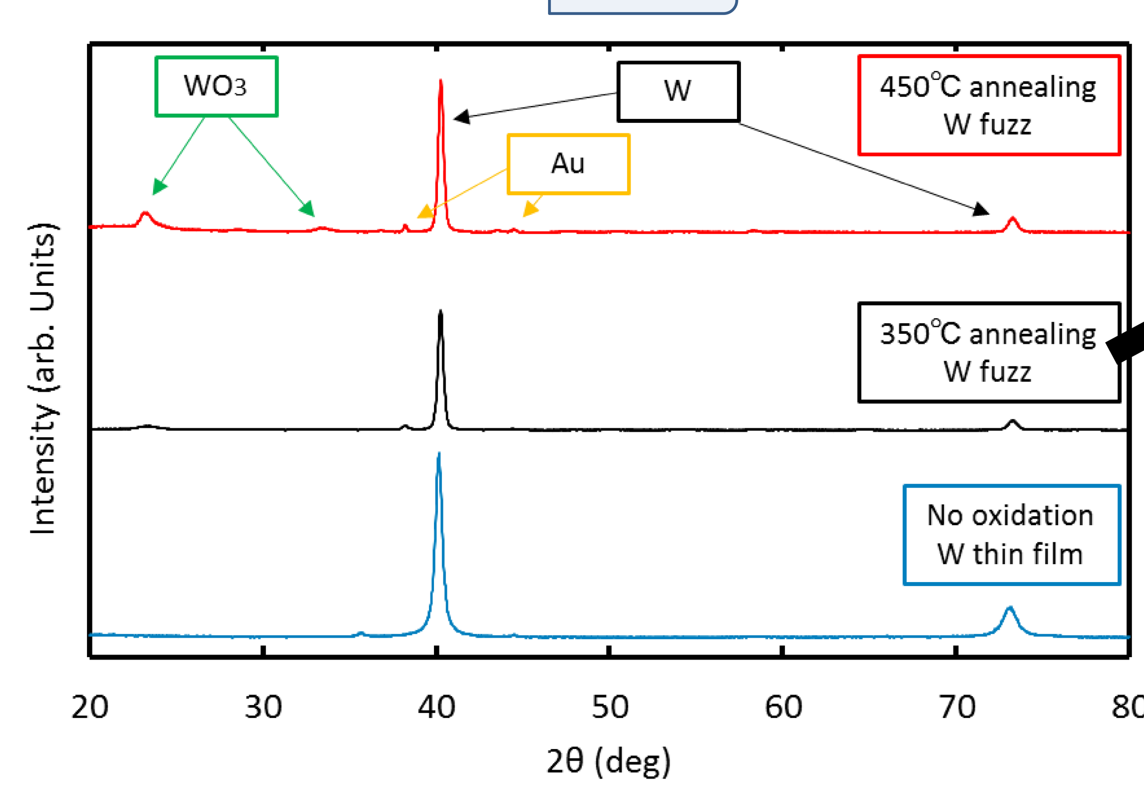


- Response curve of the W oxide with fuzz nanostructure, which is oxidized at 350°C for an hour, at operating temperature (200~400°C).
- It showed the n-type property that the resistance value decreases when H_2 gas is introduced.
- It showed a stable response at 300°C~400°C, and a change in resistance of about one order of magnitude was confirmed.

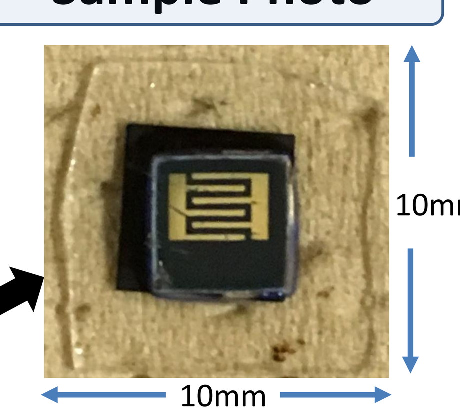
Sample Characterization

- We prepared two samples which were **1 hour annealing fuzz at 350°C** and **1 hour annealing fuzz at 450°C**

XRD

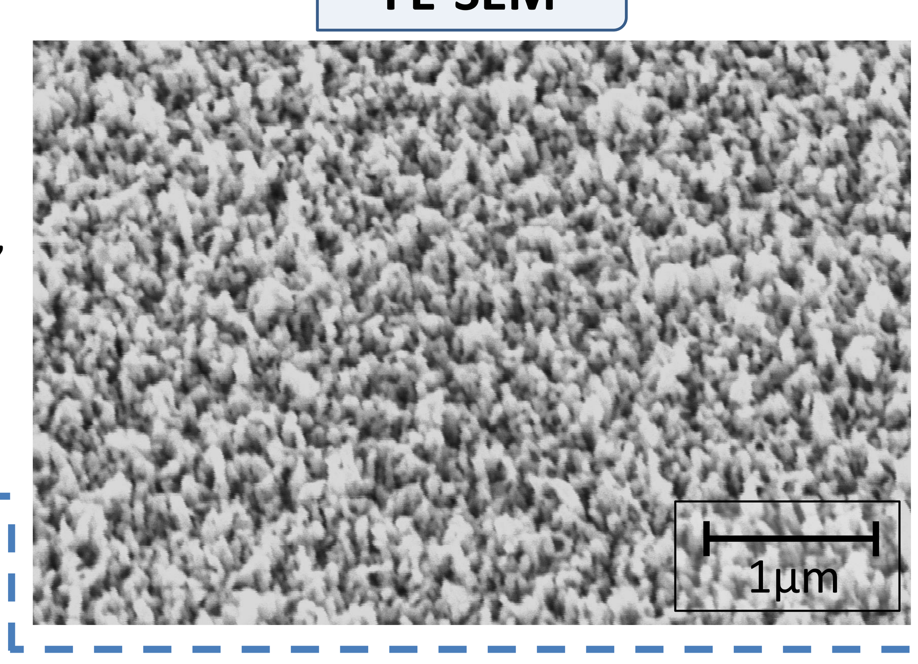


Sample Photo



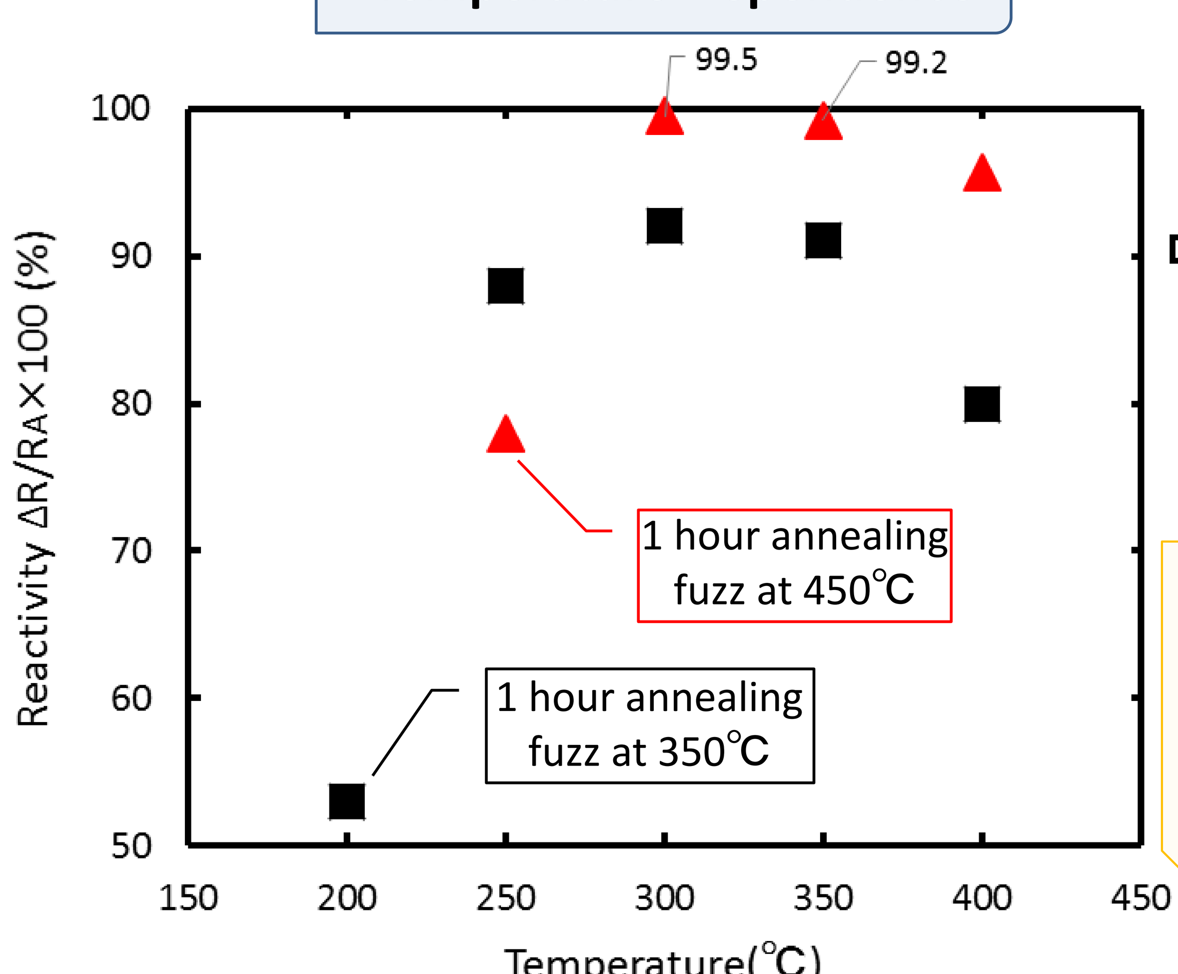
- WO_3 was confirmed in the oxidized samples from XRD results.
- Higher oxidation temperature, results in increased WO_3 formation.

FE-SEM



- Fuzz is fragile, so there was a possibility that it could be broken by oxidation and sensing, but it was confirmed that it remained by FE-SEM observation.

Temperature Dependence



- Reactivity is given by

$$\frac{R_{Air}-R_{Gas}}{R_{Air}} \times 100(\%)$$

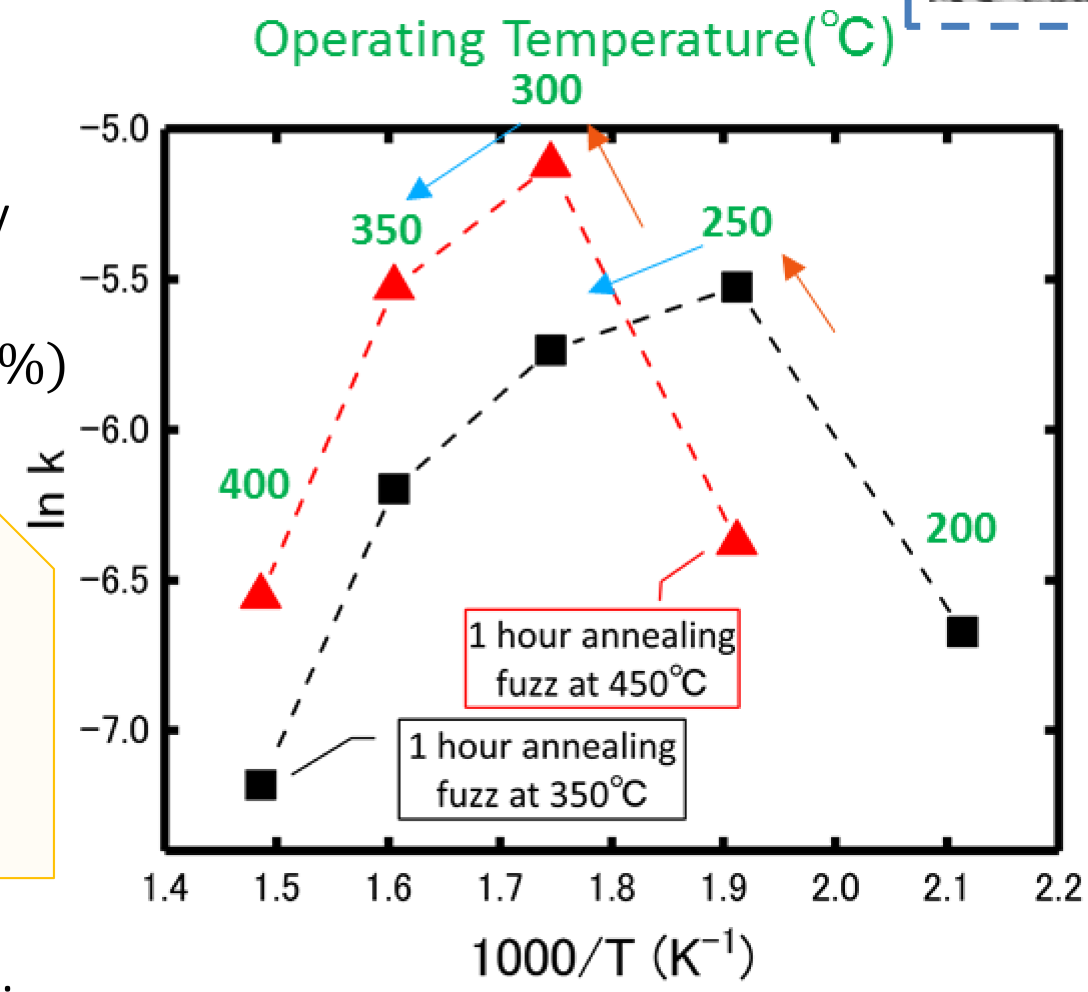
R_{Air}:Resistance after exposing to air

R_{Gas}:Resistance after exposing to hydrogen gas

- The largest change in temperature at 300°C was confirmed in both samples.
- W fuzz oxidized at 450°C showed the reactivity of **99.5%**.

Lower gas concentration can be detected

Arrhenius plot



- Relation(H_2 adsorption, diffusion, chemical reaction, etc.), being the slowest determine the response kinetics.
- Assuming that the response can be indicated by primary kinetics the conductance transients[$G(t)_{response}$] is given by

$$G(t) = G_0 \exp(-kt).$$

This response rate constant (k)

$$k = k_0 \exp(-E_a/2k_B T),$$

E_a is the activation energy.

- According to the slopes(E_a) of Arrhenius plot from the above equation, kinks were observed at sensor testing temperature of 250°C and 300°C for low(350°C) and high(450°C) temperature annealed specimens respectively. These kinks represent changes of dominating reactions during H_2 sensing.