Hydrogen sensing properties of nanocomposite NiO:Au and NiO:Pd thin films at ppb-concentration levels

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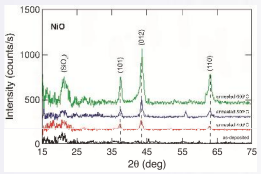
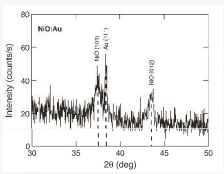
Abstract

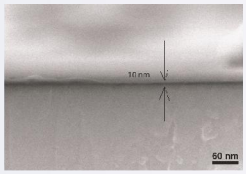
Hydrogen finds increasing applications in industry and transportation as a clean fuel, therefore smart hydrogen sensors with high sensitivity are essential. We present results on the fabrication of p-type NiO:Au and NiO:Pd thin-film resistive nanocomposite sensors, which are able to detect hydrogen in air at ppb-level concentrations, operating at low temperatures. Even though in general p-type sensors have smaller response signals than n-type sensors, we achieve high performance with nanocomposite p-type NiO sensors. Therefore, we can take advantage of the excellent chemical stability [1] and ease of fabrication of NiO.

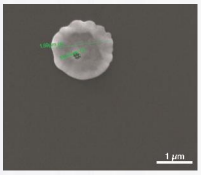
Thin NiO films were deposited by sputtering on silicon and quartz substrates. The film surface was partially covered with Au or Pd nanoparticles by employing Pulsed Laser Deposition (PLD) of metallic targets, using an Nd:YAG laser (10 ns pulse duration) operating at 355 nm. Because NiO is a p-type semiconductor, its electric resistance increases in the presence of hydrogen, which is a reducing gas [2].

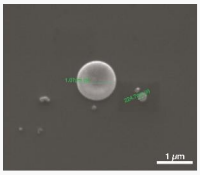
NiO:Au





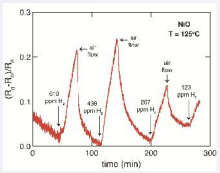


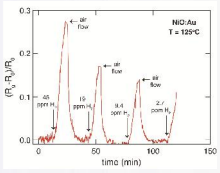


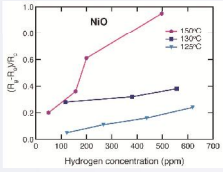


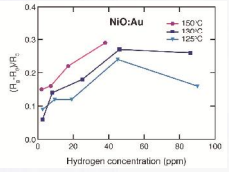
- X-ray diffractograms: the as-deposited film is amorphous, while annealing induces partial crystallization in the material.
- NiO films deposited with similar conditions to those employed in this work were found to be rhombohedral [3].
- From the Scherrer equation we estimate the average size of the NiO grains at 15 – 20 nm and the Au nanoparticles at ~77 nm.
- SEM image of a NiO film in side view and SEM images of NiO films after Au deposition.

Hydrogen sensing



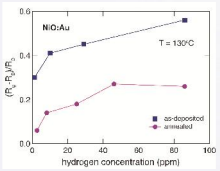


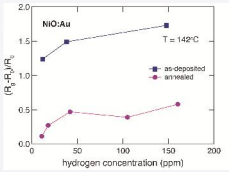




- The presence of Au nanoparticles allows for the detection of two orders of magnitude lower hydrogen concentrations.
- The response time of the sensor (defined as the time interval between 10% and 90% of the total signal change) decreased from ~15 min to ~5 min after Au deposition.
- Au nanoparticles act as catalysts and also increase the effective sensor area.

Effect of annealing





- The response of the as-deposited NiO film was compared with the response of the film annealed at 400°C, after Au deposition.
- The as-deposited sample shows increased response compared to the annealed sample.
- NiO is a p-type semiconductor due to the O-interstitial defects. Annealing of the NiO samples improves their quality and decreases the defect density, therefore their performance as sensors declines.

References

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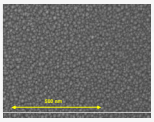
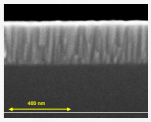
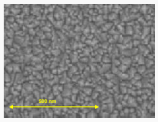
2. I. Fasaki *et al.*, "Nickel oxide thin films synthesized by reactive pulsed laser deposition: characterization and application to hydrogen sensing," *Appl. Phys. A* **91**, 487 (2008).
3. I. Hotovy , J. Huran, and L. Spiess, "Characterization of sputtered NiO films using XRD and AFM," *J. Mater. Sci.* **39**, 2609 (2004).

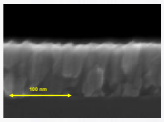
NiO:Pd





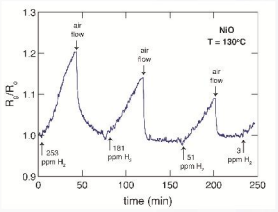
- NiO thin film sputter-deposited with 33% O_2 in Ar at 300°C.

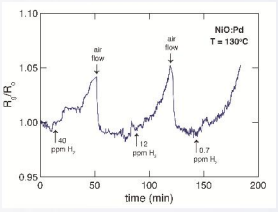


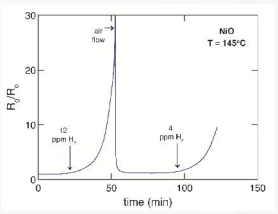


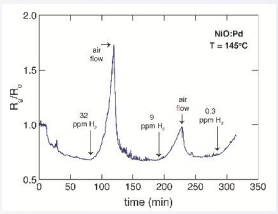
- NiO thin film sputter-deposited with 80% O_2 in Ar at room temperature.

Hydrogen sensing









- Prior to Pd deposition, the samples are capable of detecting hydrogen concentrations as low as 3-4 ppm in air.
- After Pd deposition, the samples detect hydrogen concentrations below the 1 ppm limit, down to 300 ppb.
- The presence of Pd nanoparticles also reduces the response time of the sensor.

Sample ID	O_2 content (%)	Pd nanoparticles	Lowest detectable H_2 concentration (ppm)	T (°C)
NiO1	32	No	5	130
		No	4	143
		Yes	0.7	145
NiO2	80	No	3	130
		Yes	0.7	130
NiO3	33	No	4	145
		Yes	0.3	146

Conclusions

- High quality nanocomposite NiO:Au and NiO:Pd thin films were prepared by a combination of sputtering and pulsed laser deposition.
- The lowest detectable hydrogen concentration decreased by two orders of magnitude, while the response time also decreased by a factor of three in the presence of metallic nanoparticles.
- Metallic nanoparticles act as catalysts and also increase the effective sensor area.
- Post-deposition annealing proved detrimental for sensing because it decreases the density of NiO defects, which act as hydrogen absorption sites(???)

Acknowledgements

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