Nanocomposite NiO:Au hydrogen sensors with a few ppm sensitivity and low operating temperature

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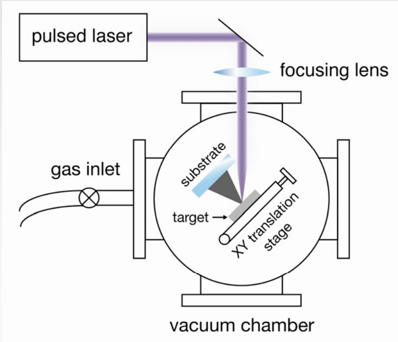
Abstract

We present results on the fabrication of p-type NiO:Au thin-film sensors, which are able to detect hydrogen in air at concentrations down to 1 ppm, operating at low temperatures (120 – 140 °C). Thin NiO films were deposited by DC sputtering on Si/SiO_2 substrates and tested as hydrogen sensors. The response of the films was drastically improved by depositing Au nanoparticles on the surface, employing Pulsed Laser Deposition.

The presence of Au on the NiO films was confirmed by EDX measurements. The effect of annealing was investigated by comparing as-deposited NiO samples with samples annealed at 400 and 500 °C. The nanomechanical properties of the films were studied by nanoindentation, showing that annealing results in films with decreased hardness and increased elastic modulus due to recrystallization. The annealed samples were able to detect hydrogen at lower operating temperatures compared to as-deposited samples.

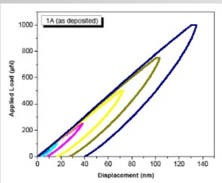
Pulsed Laser Deposition

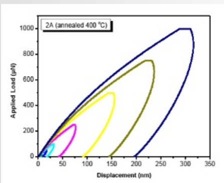


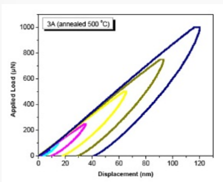
- Q-switched, Nd:YAG laser system, 355 nm, 8 ns pulse duration.
- Deposit Au nanoparticles on DC-sputtered NiO films on Si/SiO_2 substrates.
- NiO films were 10 nm thick. Prior to Au deposition some films were annealed at 400 and 500 °C for 1h in N_2.
- Annealing results in decreased hardness and increased elastic modulus due to recrystallization.
- Control of concentration of Au nanoparticles on the NiO surface by adjusting the laser fluence and deposition time.
- Response to hydrogen was drastically improved by depositing Au nanoparticles.

Nanoindentation

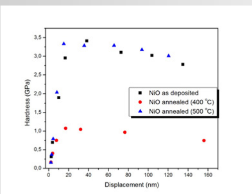
- The nanomechanical properties of the films were evaluated by nanoindentation.
- The nanoindentation tests were performed using a Hysitron TriboLab® Nanomechanical Test Instrument, equipped with a Berkovich tip (120 nm tip radius), which allows the application of loads from 1 to 10000 μN
- In all depth-sensing tests, a total of 10 indents were averaged to determine the mean hardness (H) and elastic modulus (E) values for statistical purposes, with a spacing of 50 μm (~45% relative humidity, 23°C).

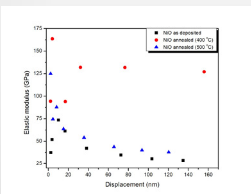






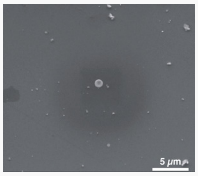
- The sample annealed at 500 °C exhibits higher resistance to applied load, *i.e.* higher applied load is needed to reach the same displacement compared to the sample annealed at 400 °C (higher hardness).
- The as-deposited sample reveals higher plasticity, *i.e.* energy stored in the material after the end of indentation (total area under curves) in comparison to the sample annealed at 500 °C.



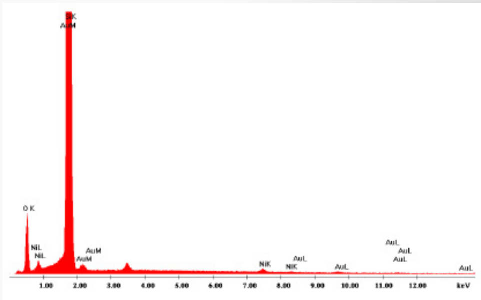


- Nanomechanical properties were obtained with the Oliver and Pharr model.
- The sample annealed at 400 °C has lower hardness values and higher elastic modulus values due to recrystallization.
- The sample annealed at 500 °C shows similar hardness with the as-deposited sample and slightly increased elastic modulus values.

Thin-film characterization

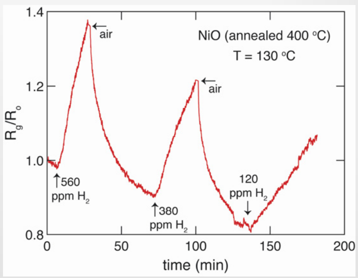


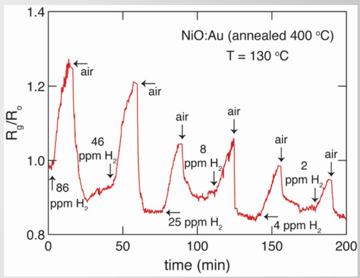
- SEM image of a NiO sample, annealed at 400 °C, with Au nanoparticles deposited by PLD.
- For Au deposition , laser pulse energy was set at 23 mJ and deposition time was 1 min.
- EDX analysis confirms Au presence.



Element	% w/w	% at.
O	76.83	96.49
Ni	4.78	1.64
Au	18.39	1.88
Total	100	100

Hydrogen sensing





- NiO is a p-type semiconductor and it resistivity increases in the presence of a reducing gas like hydrogen.
- The sample annealed at 400 °C gave better hydrogen sensing results, before and after Au deposition.
- Au nanoparticles act as catalysts for the hydrogen reaction. They increase the sensitivity of the sensor and reduce the response time.

References

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Conclusions

- Pulsed laser deposition was combined with sputtering in order to produce NiO thin films covered with Au nanoparticles.
- The as deposited NiO films were amorphous and were recrystallized after being annealed at 400 and 500 °C for 1 hour in N_2.
- The nanomechanical properties of the films were examined with nanoindentation. The film annealed at 400 °C was found to have the lowest hardness and the highest elastic modulus values.
- The film annealed at 400 °C was the best hydrogen sensor. It was able to detect the smallest hydrogen concentrations with the shortest response time.

Acknowledgements

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