Development of NiO-based thin film structures as efficient H₂ gas sensors operating at room temperatures

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P-type NiO thin films have been developed on high resistivity Si and SiO₂ substrates by a pulsed laser deposition technique using a ArF* 193 nm excimer laser at deposition temperature of 70°C and in 40 Pa partial oxygen pressure. Structures based on such NiO films as host material in the form of an Au/NiO Schottky diode have been subsequently developed under vacuum. In a different procedure, an n-SnO₂ layer has been deposited by a CVD technique on a NiO film to produce a p/n heterojunction. The sensing properties of all above structures have been tested upon exposure to a 3% H₂ in air mixture flows at various operating temperature ranging from 30 to 210°C. For the NiO films, the optimum temperature was about 150°C exhibiting a sensitivity of 94%. After surface sensitization by Au the NiO films exhibited a dramatic increase in the operating temperature of 30°C. The sensitivity of p-NiO/n-SnO₂ heterojunction devices was extracted from I-V measurements in air and under H₂ flow mixed in air. In this case a dramatic increase of the sensitivity was achieved at operating temperature of 30°C for a forward bias of 0.2 V.

H₂ sensing properties

• The H₂ sensing properties of the NiO thin films were strongly dependent on the operating temperature (Fig.1a) as well as on the surface morphology of the films.
• The response time decreases from 15 to 7 min and the recovery time changes from 2 to 1 min as the working temperature increases from 150 to 210°C (Fig.1a).
• The Rgas/Rair ratio of the NiO/Si sensor increases almost 10 times (from 2 to 40) as the working temperature changes from 150 to 210°C (Fig.1b).
• The enhanced oxidation of adsorbed hydrogen due to Au effect can be seen in Fig. 2a where the response time of the Schottky diode working at 70°C is identical to the response time of the NiO thin film working at 210°C.

Conclusions

• P-type NiO thin films have been examined as potential H₂ sensors at temperatures of 150-210°C with best results at working temperature of 210°C on (001) Si substrate while the use of SiO₂ as substrate greatly worsened the sensing properties.
• The implementation of a Schottky Au/NiO/Si diode as sensing element lowered remarkably the required working temperature even at R.T. with 8% sensitivity and response times of 7-8 min.

Abstract

The deposition of the NiO nanostructures were performed inside a stainless steel vacuum chamber. Prior to each irradiation the vacuum chamber was evacuated to an ultimate pressure of 1×10⁻⁷ mBar. The UV laser pulses generated by a Lumonics Mo: TE 861T ArF Excimer laser (λ=193 nm, τ=24 ns) was repeated at 10 Hz, with an energy of 200 mJ/cm². For the Ni targets, a laser beam was focused on the Ni target (a 99.99% metal foil) with an incidence angle of 45° relative to the normal of the target surface. To avoid fast drilling, the target was placed on the laser focus. For the Au/NiO Schottky diode, we applied the same UV laser fluence for 30 min.

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