Optical, structural and hydrogen sensing properties of TiO₂ thin films

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Abstract

TiO₂ thin films were prepared by DC reactive magnetron sputtering in a mixture of oxygen and argon on glass and oxidized silicon substrates. The effect of annealing (300–500°C, 500–700°C for 8 h in air) on the structural and morphological (XRD, EDX, AFM) properties of TiO₂ thin films is presented. In addition, the effect of Pt surface modification (1, 3 and 5 nm) on hydrogen sensing was studied. In the range of temperatures from 300°C to 500°C, crystallization starts and the thin film structure changes from anatase to polycrystalline (anatase phase). In the case of samples on glass substrate, the optical transmittance spectra were recorded and energy band gap was estimated. TiO₂ thin films were used as sensors towards hydrogen at concentrations 1000–10000 ppm and working temperatures within the range 180–200°C. The samples with 1 and especially with 3 nm Pt on the surface responded fast at with high sensitivity to hydrogen.

Characterization of the TiO₂ films

The XRD diffractogram shows that the samples without annealing and annealing at 300°C have amorphous structure, whereas the samples annealed at 500°C and 700°C show polycrystalline structure with (111) and (200) peaks in XRD diffractogram. The samples treated at temperatures 500 and 700°C show peaks representing the anatase phase of polycrystalline TiO₂ with preferential orientation in direction (101).

Hydrogen sensing

Before every sensing measurement the TiO₂ thin films were heated for 10 hours for thermal activation.

Samples without Pt overlayer did not respond to hydrogen at 200°C which was the maximum temperature used in our experiments.

All the sample with 5 nm Pt modification, the Pt layer caused a shortage in our measurements and the access of hydrogen to TiO₂ surface was problematic.

TiO₂ samples with 1 and 3 nm Pt surface modification were tested towards hydrogen concentrations: 10000, 5000, 2000 and 1000 ppm at 180, 190 and 200°C.

The sensitivity was defined as: S = (R₀–Rᵧ)/Rᵧ where R₀ is the resistance of the film in dry air and Rᵧ is the resistance of the film in the gas mixture.

The samples with 1 and 3 nm Pt showed high sensitivity towards hydrogen and the response time was several minutes. It is clear that the sensitivity of all TiO₂ sensors towards hydrogen showed a strong dependence on both the operating temperature and gas concentration. For the same operating temperature, the response of the sensors towards hydrogen sharply increased with the increase of gas concentration.

All samples showed a saturation-like behaviour in dependence on the hydrogen concentration. The temperature range 180–200°C is adequate for hydrogen detection as low as 1000 ppm. The best results were obtained by the sample with 3 nm Pt (higher sensitivity and faster response).

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