Optical, structural and hydrogen sensing properties of TiO_2 thin films

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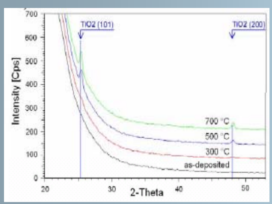
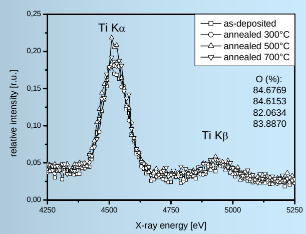
Abstract

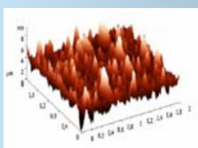
TiO_2 thin films were prepared by DC reactive magnetron sputtering in a mixture of oxygen and argon on glass and oxidized silicon substrates. The effect of annealing (300 °C, 500 °C and 700 °C for 8 h in air) on the structural and morphological (XRD, EDX, AFM) properties of TiO_2 thin films are presented. 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 amorphous to polycrystalline (anatase phase). In the case of samples on glass substrate, the optical transmittance spectra were recorded and energy band gap was estimated. TiO_2 thin films were used as sensors towards hydrogen at concentrations 10000-1000 ppm and working temperatures within the range 180-200 °C. The samples with 1 nm and especially with 3 nm Pt on the surface responded fast at with high sensitivity to hydrogen.

Characterization of the TiO_2 films

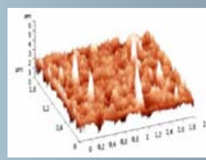




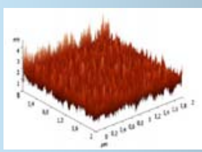
The EDX analysis showed that the Ti:O ratio increases at temperatures between 300 and 500 °C The biggest change in thin film oxygen content from 84.6 % to 82 % occurred during crystallization.



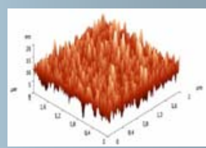
Without annealing



Annealed at 300 °C



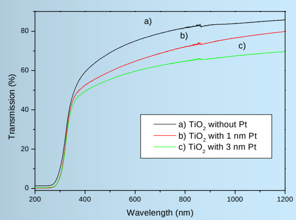
Annealed at 500 °C



Annealed at 700 °C

•The XRD diffractogram shows that the samples without annealing and annealing at 300 °C have amorphous structure, whereas the samples annealed at 500 and 700 °C show polycrystalline structure with (101) and (200) peaks in XRD diffractogram.

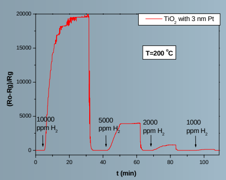
•The samples treated at temperatures 500 and 700 °C show peaks representing the anatase phase of polycrystalline TiO_2 with preferential orientation in direction (101).

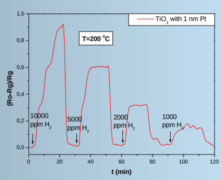


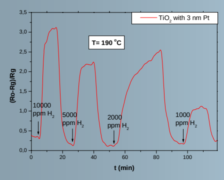
Transmittance spectra of the modified samples by 1, 3 and 5 nm Pt. The energy band gap was calculated and found to be 3,93, 3,92 and 3,91 eV for TiO_2 without Pt, with 1 and 3 nm Pt successively. A significant lowering of transmittance due to increase of Pt layer thickness was observed.

AFM measurements show a decrease of the RMS roughness with increasing annealing temperature till 500 °C. A significant difference occurs at temperature of 700 °C, where the roughness increases markedly.

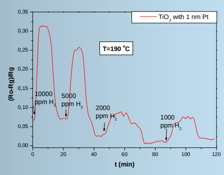
Hydrogen sensing







TiO_2 thin films with 3 nm Pt



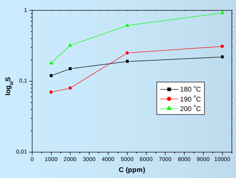
TiO_2 thin films with 1 nm Pt

•Before every sensing measurement the TiO_2 thin films were heated for 10 hours for thermal activation.

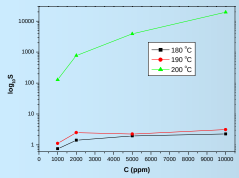
•Samples without Pt overlayer did not respond to hydrogen at 200 °C which was the maximum temperature used in our experiments.

•At the sample with 5 nm Pt modification, the Pt layer caused a shortage in our measurements and the access of hydrogen to TiO_2 surface was prohibited.

•TiO_2 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.



TiO_2 thin films with 1 nm Pt



TiO_2 thin films with 3 nm Pt

•The sensitivity was defined as: S = (Ro-Rg)/Rg where Ro is the resistance of the film in dry air and Rg is the resistance of the film in the gas/air 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 TiO_2 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).

• An optimization of DC Magnetron Reactive Sputtering parameters is in progress to decrease the operating temperature of TiO_2 thin films and cut down the response time of the developed sensors.

ACKNOWLEDGEMENTS

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