DOI 10.5162/IMCS2012/P1.7.7

Hydrogen sensing properties of nanotubular TiO_2, Al-and Cr-doped TiO_2 sensor materials

Yakup Gönüllü[1], Bilge Saruhan-Brings[1],
German Aerospace Center, Institute of Materials Research, Linder Hoehe, 51147 Cologne, Germany
Yakup.Goenuellue@dlr.de

Summary
As previously demonstrated TiO_2-nanotubes are highly sensitive to hydrogen under 300°C. Despite very fast response with relative short times was obtained, the recovery times are extremely long. Al- and Cr-doping of TiO_2-nanotubes improves the recovery of the sensors and reduces the recovery times

Key words: Anodization, TiO2, Doping, Hydrogen-sensing

Introduction

There is an ongoing need to develop hydrogen (H_2) gas sensors for industrial process control, combustion control and medical applications. Room temperature metal oxide hydrogen sensors are generally based on Schottky barrier modulation of Pd/TiO_2 or Pt/TiO_2 [1]. Currently available sensors are not sufficient to succeed high selectivity by detection of hydrogen gas above 500°C [2]. Titania (TiO_2) is one of the most promising sensor materials for development of highly sensitive hydrogen sensors. It is low cost and non-toxic and has gained much attention owing to its high stability at elevated temperatures and in harsh environments. The nano-tubular structure formation on metallic titanium and some titanium alloys with electrolytic processes have improved the sensing and selectivity characteristics of titania-based hydrogen gas sensors [3]. Since the nanostructuring will provide larger surface area with high aspect ratio, nanotubular TiO_2 achieved by electrolytic processing of metallic titanium opened up new horizons for increasing the sensing characteristics of titania-based gas sensors. Doping TiO_2 with aluminum enhances selectivity towards hydrogen sensing [2].

In this present study, nano-tubular undoped TiO_2, TiO_2 doped with Al and Cr have been synthesized using both anodic oxidation process and sol-gel technique. These materials have utilized as sensor materials in hydrogen sensing measurements. The resistance changes of these nano-tubular sensors have measured under different concentrations of H_2 in order to investigate the concentration dependence of sensor response.

Experimental Methods

Un-doped TiO_2nano-tubes were grown on the commercially pure titanium foil (99.6 %) via anodization method. Mirror polished Ti foil substrates with a thickness of 0.25mm was subjected to porous anodization process in two different solutions; an Ethylene Glycol (EG)-based electrolyte with 98 vol. % EG, 2 vol. % H_2O and 0.3 wt. % NH_4F using an anodization voltage of 60V (Fig. 1).
For doping with Cr, the nanotubular samples were rinsed with ethanol, dried in static air prior and then dipped in Cr^{3+}-solution in vacuum atmosphere. A saturated Cr_{3+} solution was prepared by dissolving $Cr(NO_3)_3*9H_2O$ in distilled water. Al-doped TiO_2 nanotubes were achieved by anodizing Ti6Al4V alloy in same solution at room temperature. The gas sensing properties of the none-doped and doped nano-tubular TiO_2-layers were determined by means of DC resistance measurement using two platinum circuits which were deposited on the layers by sputtering. The gas sensing measurements of the nano-tubular TiO_2 layers were carried out at 300°C in a Carbolite furnace. The change in resistance of the TiO_2 sensor devices were measured upon exposure to H_2 under constant voltage and at respectively H_2 concentrations of 50, 75 and 100 ppm in argon atmosphere.

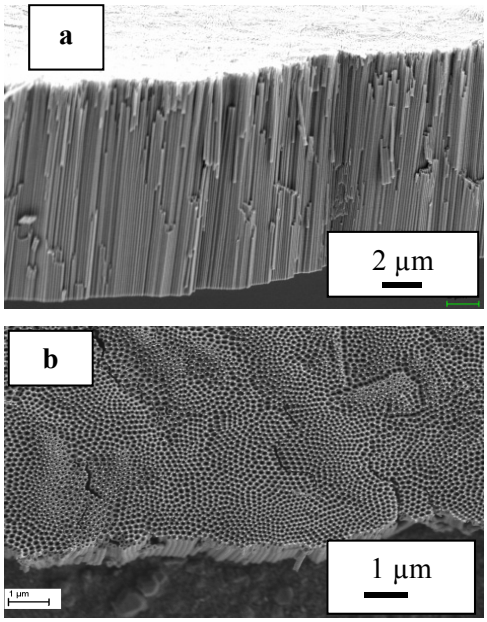

Fig 1.Cross section (a) and surface of TiO_2 nanotubular layer (b) after annealing process.

Results

In TiO_2, Cr-TiO_2, Al-TiO_2nano-tubular sensors exhibited good response towards all tested concentrations (50-100 ppm in Argon) of H_2 gas, as indicated with the sudden decrease of resistance on release of H_2 gas. This behaviour can be attributed to the highly-ordered nano-tubular oxide structures achieved on anodization of Ti and Ti alloys. These nanostructures allow better interaction between hydrogen gas and sensing material and extensive diffusion of hydrogen gas molecules, relying on larger surface area and nano-porosity as well as easier crystallization kinetics of the electrode material. The concentration dependent responses are fast, repeatable and stable. However, the recovery times are long and in some cases, the saturation cannot be fully achieved after ceasing the H_2 gas flow. This property seems to be improved on doped TiO_2nano-tubular electrodes. Aluminum and Cr-doped nano-tubular TiO_2-sensors are proved to have better recovery behavior with shorter recovery times over nano-tubular undoped TiO_2 sensor presumably due to the doping induced p-type semiconductor property. Al-TiO_2 exhibit more promising sensor behavior towards hydrogen.In TiO_2, Cr-TiO_2, Al-TiO_2nano-tubular sensors exhibited good response towards all tested concentrations (50-100 ppm in Argon) of H_2 gas, as indicated with the sudden decrease of resistance on release of H_2 gas.

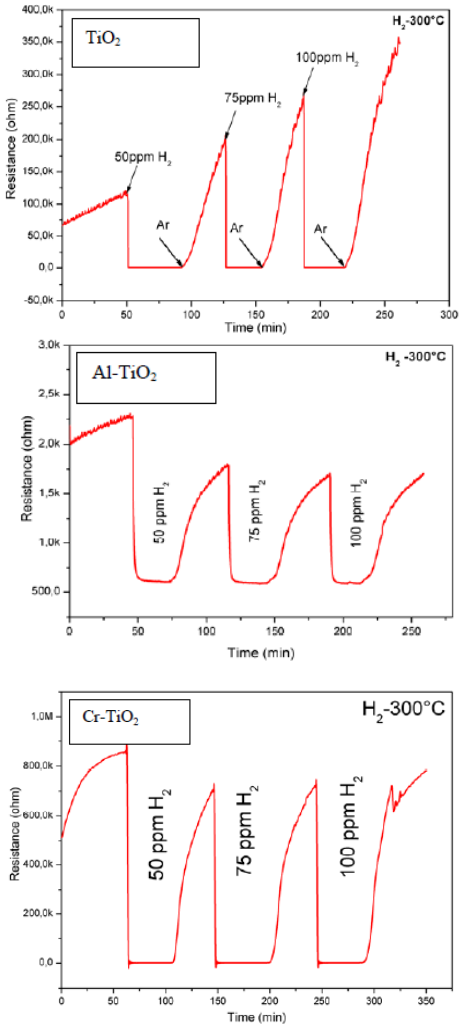

Fig. 2: Sensor response of nanotubular TiO_2, Al-doped TiO_2 and Cr-doped TiO_2 under H_2 concentrations of 50, 75, 100 ppm at 300°C

This behavior can be attributed to the highly-ordered nano-tubular oxide structures achieved on anodization of Ti and Ti alloys, allowing better interaction between hydrogen gas and sensing material and extensive diffusion of hydrogen gas molecules. This diffusion behavior is in turn the reason for long recovery times. Although, the concentration dependent responses are fast, repeatable and stable, the recovery times are long and even in some cases, the saturation cannot be fully achieved after ceasing the H_2 gas flow. This property seems to be improved on doping TiO_2nano-tubular electrodes. Al- and Cr-doped nano-tubular TiO_2-sensors exhibit better recovery behavior with shorter recovery times over nano-tubular undoped TiO_2 sensor presumably due to the doping induced p-type semiconductor property. Al-TiO_2 exhibits more promising sensor behavior towards hydrogen.

DOI 10.5162/IMCS2012/P1.7.7

References

[1] Kobayashi, K. Kishimoto, Y. Nakato, *Surf. Sci.,* 306, 393 (1994).

[2] D. Birkefeld, A.M. Azad, S.A. Akbar, *J. Am. Ceram. Soc.,* 75, 2964 (1992).

[3] O.K. Varghese, D. Gong, M. Paulose, K. G. Ong, C.A. Grimes, Sens. and Actuators B, 93, 338-344 (2003).