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Hydrogen gas sensing properties of nanoporous Al-doped titania

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ABSTRACT

Nanoporous aluminum doped titanium (TiAl) oxide thin film sensor materials with an Al concentration of 9–10 at.% were produced on alumina substrates and their hydrogen (H_2) sensing behaviors were investigated. The well-adherent and dense metallic TiAl thin films with equiaxed structure were deposited on alumina substrates using cathodic arc physical vapor deposition (CAPVD) method and the nanopores were grown on the TiAl thin films by anodic oxidation in ammonium fluoride (NH_4F) containing ethylene glycol (EG) electrolyte. With the deposition method utilized, it became possible to anodize the films without spalling and defects. The metallic film on alumina was totally anodized in order to eliminate short-circuit problems between the metallic layer below the oxide and Pt pads used for resistance measurements. The amorphous nanoporous structures were converted into anatase by heat treatment at 480 °C for 3 h and the fabrication of sensor was completed by depositing Pt contact pads on the surface of nanopores using magnetron sputtering technique. The hydrogen sensing performance of thin film nanoporous TiAl oxide sensor was studied in the range of 50–2500 ppm hydrogen at different temperatures (25–350 °C). The sensor characteristics in terms of sensitivity, response, recovery and stability were examined in detailed analysis and a possible hydrogen detection mechanism was proposed. The nanoporous TiAl oxide sensor exhibited promising sensing performance towards H_2 gas concentrations and quick response and recovery behavior with high stability.

1. Introduction

Metal oxide semiconductor sensors are reliable, fast, cheap and low maintenance devices widely used for a variety of gas sensing applications. Increasing demands of the industry (higher sensitivity, stability and selectivity) forces further developments in this field. Two major routes for improving the performance of metal oxide sensors are doping them with other metals, oxides and reduction of grain size to nanometer level. By doping, electronic structure or catalytic properties of the sensor can be modified for better performance [1–3]. On the other hand by nanostructuring of the sensor material specific surface area can be extended along with the approaching of the grain sizes to Debye length both of which result in a higher sensitivity of the sensor [4].

One of the most popular metal oxide semiconductors is titanium dioxide. Titania is a wide band gap semiconductor with two polymorphs, anatase and rutile, that may exhibit n and p-type semi conductivity depending on its primary particle size, dopants, band gap and heat treatment temperature [1,5–7]. In the literature there are many studies concerning the utilization and increasing the sensitivity of titania based sensors by the above stated approaches [1–4,8–13]. A wide variety of dopants (Cr, Nb, Cu, Sn, Zn, Ag, Fe, La, Ta, Y, Al, V, NiO_x, Y_2O_3, WO_3, MoO_3, V_2O_5, Ga_2O_3, ErO_3, Ta_2O_5) have been used for modifying charge carrier concentration, surface potential, chemical composition and crystal size of TiO_2 based sensors [1,8,10,14,15]. The most important development in the performance of TiO_2 based sensors was observed when the crystal size is reduced to nanometer level [4]. Recently porous anodization of titanium and doped titanium became a popular approach for benefiting both from dopant effects [1–3] and nanostructuring [4,12,13].

This study aims to produce nanostructured and doped titania based hydrogen sensors on ceramic substrates. Although there are various studies on the hydrogen sensing properties of nanostructured titania in the literature [4,12,13], there are limited number of studies on hydrogen gas sensing properties of doped TiO_2 nanostructures. In these studies Pd and Pt nanoparticles are introduced into the nanotubular titania films as catalyst since these dopants favor the adsorption and dissociation of hydrogen

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molecules and thereby resulting in the spill-over of the reaction products onto the surface of the TiO_2 semiconductor [4,8,16–19]. In this study aluminum is selected as the doping element since this dopant is expected to improve the sensing properties by increasing the conductivity [20–23], decreasing grain growth [1,20,23,24] and increasing the temperature of anatase to rutile conversion [1,23–26].

In the majority of the studies that utilize titanium anodic oxides as sensing materials, titanium and titanium alloy sheets or foil substrates are used. These structures are composed of a titanium metal substrate and a porous oxide that is produced by anodization. In cases where high temperature utilization of these sensors is required, the continuing oxidation and corrosion of the metallic substrate may result in the degradation of the sensor. There are limited numbers of studies in the literature that are related to anodization of titanium coated ceramic substrates [27–30]. Production of sensor materials by anodization of titanium and doped titanium that are deposited on ceramic substrates is preferable since it is more economical, flexible with respect to preparation of the films with different dopant concentrations and more suitable for incorporation into standard fabrication processes of devices [4,29,31]. However, in these studies, method of deposition, stability during anodization process, structure and the morphology of the coatings and the adhesion problems that limits the thickness of the anodic oxide layers are mentioned as bottlenecks of the approach [4,27–29].

Thus for fulfilling the aims of this study:

development of a deposition method for the production of thick, well adherent, anodizable metallic coatings on alumina substrates. optimization of the anodization process for the coatings used in the sensor application are required. For this purpose a modified CAPVD process was utilized for coating of the alloys [32] and the produced coatings were anodized with the pre-determined optimized parameters for TiAl alloys [33] in order to obtain TiAl oxide nanopores on alumina substrates.

2. Experimental

TiAl thin film coatings were produced on alumina substrates (Kyocera, 50 mm × 25 mm in size) using a CAPVD instrument (Novatech-SIE, Model: NVT-12). For the production of TiAl coatings, a TiAl cathode containing 25 at.% Al was used. Since the applied bias voltage was effective on the coating composition, the coatings were deposited at different bias voltages (0 V, 100 V, 150 V, 200 V). EDS (energy dispersive spectrometer) results showed that the Al content of TiAl layer changed depending on the applied bias voltage. According to EDS results, the amount of Al in TiAl coating deposited at 0 V gave a similar composition to the cathode material. However, with the increase of bias voltage, the amount of Al in TiAl gradually decreased due to the higher sputtering rate of Al. The coating with homogeneous Al content of 9–10 at.% was achieved with depositing the films at 100 V bias voltage and subsequent high bias voltage post treatment applied after deposition. The composition of the deposited metal layers was analyzed by EDS attached to scanning electron microscope (SEM).

Prior to the deposition process, the alumina substrates were cleaned and preheated up to 850 °C by applying pulse DC bias voltages of −600 V, −800 V and −1000 V, subsequently. Then TiAl coatings were deposited under −100 V DC bias voltage using 60 A cathode current for 20 min. During the deposition 20 sccm Argon gas was given to the system for a stable operation of the cathode. Substrate temperature was kept in a range of 450–600 °C during the deposition. At the end of deposition, bias voltage was increased to −400 V for duration of 4 min for heating the deposited alloys to 850–900 °C. This process is used for densifying the coating structure and homogenizing the composition. The chemical composition of the deposited films was determined by using SEM with EDS attachment.

Before anodization TiAl coating surfaces were chemically etched for 5 s in a mixed solution of 19 vol.% hydrofluoric acid (HF), 46 vol.% water (H_2O) and 35 vol.% nitric acid (HNO_3) and subsequently the coating surfaces mechanically polished using 320, 500, 800, 1000, 1200, 2400, 4000 grid SiC papers sequentially for further polishing of the surface. This process has been conducted for smoothing of the surface and removal of the macroparticles that are produced during CAPVD deposition of the metal layers. These macroparticles present as asperities on the surface and removal of these macroparticles is necessary for overcoming their unfavorable effects (uneven current distribution, precipitation of fluorides) during anodization. The as deposited thickness of the films was 8–10 μm. During the polishing process 2–3 μm of the film was removed leaving back a 5–6 μm metallic layer with a smooth surface.

Anodization process was performed in ethylene glycol electrolyte consisting 0.25 wt.% NH_4F and 1.6 vol.% H_2O at 60 V and 21 °C for 40 min. These parameters for anodization of TiAl alloys were selected in the light of a previous study conducted within our research group [33]. The anodized TiAl nanopores structures were then subjected to heat treatment at 485 °C for 3 h to obtain anatase structure.

Specimens were characterized using JEOL JSM_7000F field emission gun scanning electron microscope (FEG-SEM). Al contents were determined by energy dispersive spectrometer (EDS) attached to FEG-SEM. The structure of coatings was analyzed using Philips PW 3710 X-ray diffractometer (XRD) and a micro-Raman spectroscope (LabRam 800, Horiba Scientific, Jobin Yvon, France).

During XRD measurements of thin films, the contributions from substrate can overshadow the XRD pattern of the thin film if standard teta-2teta measurements were used. Therefore, for the XRD analyses of the samples, glancing angle X-ray diffraction (GAXRD) was used. In this type of measurements, X-rays are sent to the sample surface with a fixed angle of incidence to avoid deeper penetration of X-rays. In this study Cu Kα radiation and an incidence angle of 2° was used for the measurements.

In micro-Raman analysis, the excitation source was a He–Ne laser with 632.8 nm line and 50× objectives was used to focus the laser beam. The beam diameter was approximately 1 μm and the laser power on the sample surface was 3 mW.

Pt contacts (13 mm × 2 mm in size) were deposited on the surface by magnetron sputtering of high purity 2 in Pt targets at 100 W for duration of 60 s. The areas other than contact pads were covered using aluminum metal mask. The spacing between the two parallel Pt contact pads is 2 mm. Before conducting sensing measurements Pt wires were connected mechanically to these pads.

The sensor measuring system consisted of a cylindrical AISI 310 stainless steel 1500 cm^3 volume chamber that is heated to the required test temperature in a tube furnace. A stainless steel spiral was connected to the gas-feeding end of the chamber for heating the gas prior to reaching the sensor. After placing the fabricated sensor into the chamber, the outlet end of the chamber is closed with a cap. A 6 mm diameter stainless steel tube was welded to the gas outlet hole of the cap. The three holes (1 mm diameter) on the cap served as feedthroughs for Pt and thermocouple wires. The temperature in the test chamber was measured by using an additional K-type thermocouple that was placed in close proximity to the samples. During the sensor tests, the resistances of sensor elements were measured by computer-controlled high resistance electrometer (Keithly 6517B). A constant bias voltage of 1 V was applied to the sensors during the measurements. The resistances of sensor electrodes were measured first under air ambient and then in a mixture of predetermined amount of hydrogen gas and