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Platinum–zirconium composite thin film electrodes for high-temperature micro-chemical sensor applications

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ABSTRACT

Stable metal interconnect thin films are critical in the development of various micro-machined devices that may operate continuously at elevated temperatures. The main objective of this work was to investigate the microstructural and electrical stability of a functionally gradient platinum (Pt)–zirconium (Zr) composite thin film electrode designed for resistive-type chemical sensors. Thin film electrodes were fabricated using a DC magnetron sputtering process. Zirconium was used as both the conventional adhesion promoter and the Pt grain modifier within the bulk electrode microstructure. The thin film deposition was completed on highly polished alumina substrates at 200 °C. The various composite Pt thin films were further annealed at 1200 °C after deposition for 1–24 h for rapid evaluation of the microstructure stability. This temperature was chosen since the electrodes are expected to operate beyond 1000 °C for high-temperature MEMS applications. Scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) were conducted to characterize the alterations in chemistry, microstructure and distribution of the constituent elements through the film thickness. The electrical resistivity of the as-deposited and thermally processed Pt thin films was measured by utilizing a van der Pauw's four-point probe technique. The work identified a Zr/Zr + Pt/Pt composite thin film with the 525 nm total film thickness that demonstrated resistivity $<5.08 \times 10^{-7}\ \Omega$ m after being processed to 1200 °C for 15 h. A lift-off technique was finally used to produce a micro-electrode patterns with the optimized film structure for high-temperature applications.
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1. Introduction

Thin films of noble metals (platinum (Pt), palladium (Pd), ruthenium (Ru), rhodium (Rh)) have widespread applications in various devices such as electrodes for chemical and electromechanical sensors and devices [1–5]. In addition, these noble metal films have found applications in high-temperature sensor applications as the elements for micro-hot plates and electrodes for structural monitoring sensors and thermocouples for harsh-environment energy applications (such as gas turbines and fuel cell systems operated at >500 °C) [6–15]. Moreover, these noble metal films are also utilized to produce embedded electrodes within various electrical components, where chemical and microstructural stability is required during the thermal processing steps; examples of these include low-temperature co-fired ceramic (LTCC) microelectronic devices and multilayer piezoelectric/electrostrictive actuators and capacitors [16–24].

The application of interest for the current work is the development of resistive-type chemical microsensors that function at temperatures >500 °C for in situ monitoring of gas compositions within solid-oxide fuel cells and coal gasifiers. There are many publications on the fabrication and operation of resistive-type gas microsensors for applications from room temperature to ∼400 °C, but literature is sparse for operation beyond this temperature range. One reason for this is limitation is due to the stability and the change in the electrochemical sensing mechanism for the sensing nano- and micro-materials at these temperatures. A second limitation is the ability to pattern and stabilize microelectrodes that can operate within these harsh environments for extended periods. Resistive-type chemical microsensors based on porous oxide semiconductor films in contact with an interdigitized electrode (IDE) pattern are the most researched and developed sensor architecture. The stability of the electrical contact between the IDEs and the sensing material during sustained high-temperature operation is of prime importance in order to maintain operation with high sensitivity, low signal drift, and low noise.

Among the noble metals, Pt is well-suited for high-temperature or corrosive environment applications and would be the electrode

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materials of choice for this application, since it possesses a high melting point and is resistant to oxidation and chemical reaction. However, Pt has several drawbacks especially processed or operated at high temperatures (≥800 °C), where the metal demonstrates a high level of coarsening/agglomeration and weak adhesion when deposited on oxide or nitride surfaces, such as those typically utilized in microsensor and MEMS designs (such as Al_2O_3, SiO_2, Si_3N_4) [25,26]. In other words, upon exposure to high temperature processing or operation, thin Pt films uncover the underlying oxide or nitride substrate, and the film separates into a discontinuous array of islands.

Platinum thin films are usually deposited by sputtering methods at relatively lower temperatures which is far from the thermodynamic equilibrium conditions for the film microstructure [27]. The low temperature sputtering for platinum is attractive since it enables the use of a simple lift-off process for device patterning. The lift-off process is preferred for Pt since the noble metal has a high chemical stability which makes it difficult to pattern by wet-etching, and dry-etching techniques are not conducive to low-cost production [28]. Unfortunately, the high temperature exposure of these sputtered Pt films usually results in the evolution of the microstructure due to typical dewetting, coarsening and sintering mechanisms which are all driven by the high surface energy of the microstructure (due to the fine microstructure and high defect concentration). In the end, the alteration and evolution of the Pt film microstructure results in decreased electrical functionality. Several strategies to address the high-temperature stability issues of the sputtered films have been proposed by various researchers. Budhani et al. first presented a strategy where an interface modification film was deposited between the oxide surface and Pt thin film. The microstructure was partially stabilized by introducing a 20–30 nm Pt_xO_{1-x} intermediate layer (or adhesion layer) through an oxidation process before subsequent Pt deposition [29]. The controlled oxidation of the thin Pt layer was also realized more recently by other researchers due to its promise for enhanced wetting and adhesion [30–33]. Other researchers utilized alternative adhesion promoters with different thicknesses, such as 10, 20, 30, 50 nm Ti (titanium), Ta (tantalum), and Zr (zirconium) films between the 360, 240, 400, 100 nm thick Pt film and the ceramic substrates. Nanometer thick films of these compositions alleviated issues with dewetting or hillock formation to a certain extent at relatively moderate temperatures [25,30,34,35]. Alloying or the incorporation of oxide inclusions within the Pt thin film (or bulk) were also shown to improve the high-temperature durability of the Pt thin films [37–39]. In addition, researchers investigated methods of incorporating alternating metal and metal oxide layered compositions into the bulk Pt thin film in order to limit sintering/coarsening processes by pinning the Pt grain boundaries [40–42]. More recently, Çiftyürek et al. utilized 35 nm thick Hf as an adhesion promoter with multiple 10 nm thick Zr as a grain pinning phase for Pt thin films for high temperature chemical sensor applications; the adhesion layer enhanced Pt bonding through the formation of intermetallic phases, and the layer-by-layer deposited Pt thin film showed a durable microstructure up to 48 h at 1200 °C [26].

The main focus of this work was to further suppress the granular sintering/coarsening mechanism at temperatures ≥800 °C for the low-temperature sputtered Pt thin films using a relatively simple and versatile sputtering process. The current work was initiated by re-evaluating the thermal stability of sputtered Pt films utilizing common adhesion promoters such as Ti and Zr over an alumina (Al_2O_3) substrate. The initial work was then used to compare against an alternative DC sputtering process used to manipulate the microstructure and thickness of the Zr adhesion layer, where a gradient in Zr concentration was varied throughout the thickness of the Pt film. By manipulating the deposition parameters (such as sputtering power and primary deposition gas pressure) during the adhesion layer deposition a functionally gradient composite Zr/Pt film was formed that demonstrated similar stability as the Zr-Pt layer-by-layer structure demonstrated by Cunha et al. [43] and Çiftyürek et al. [26]. After a high-temperature stable, composite Zr/Pt film was proven, a method for fabricating the required micro-IDE pattern for sensor applications was demonstrated; this development was important since both Zr and Pt are not easily etched, especially through wet-chemical techniques. This work was realized by using a modified lift-off process for patterning the Zr/Pt composite electrode using the optimized adhesion promoter structure and thickness. The high temperature stability of the composite thin films, as well as, the patterned microelectrodes were tested at 1200 °C for various isothermal hold times, which is far beyond the temperature range typically used for chemical and electromechanical microsensors.

2. Experimental

A magnetron sputtering technique operated (CVC 610 DC Magnetron Sputtering Station) at 100 W with a primary gas (argon) pressure of 50 mTorr for Ti and Zr adhesion films and the primary Pt electrode film (unless otherwise indicated). The films were deposited upon polycrystalline Al_2O_3 substrates with a surface roughness (R_a) of ∼35 nm. All adhesion layers were deposited to the same 50 nm thickness, as well as, the Pt layer with 425 nm in thickness (unless otherwise indicated), in order to provide consistency among the deposited thin films. The film thicknesses were measured with a Tencor Alpha-Step 200 profilometer with an accuracy limit of ±3 nm. The sputtering chamber was sustained with a base pressure of 1×10^{-7} Torr, and 2 in. sputtering targets were utilized.

The post-deposition annealing was completed at 1200 °C in a conventional tube furnace (MTI GSL 1600X) in order to mimic potential high temperature operation conditions. A 5 K/min heating and cooling rates were chosen. The annealing time was varied from 1 to 24 h under a N_2 atmosphere (with a O_2 and H_2O content of 2 ppm and 3 ppm, respectively) in order to characterize the microstructural evolution due to grain growth and sintering processes for the adhesion and composite films. In order to evaluate the thin film microstructure, the film surfaces were examined using a scanning electron microscopy (SEM, JEOL 7600 F). Energy-dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS, PHI 5000 Versaprobe) were utilized in order to determine the surface composition and chemical state of the elements, and the XPS unit was later used for depth profiling of the films. The EDS spectra were obtained using an Oxford INCA attached to JEOL 7600FE-SEM. The XPS source was operated at 15 kV and 25 W using Al Kα (1486.6 eV) radiation. The films were analyzed by a combination of 117.40 eV survey scans and 23.50 eV detailed scans of peaks of interest. A 0.5 eV step was used for each survey scan and a 0.05 eV step for the detailed scan. Prior to spectral analysis, all coating surfaces were cleaned against atmospheric and post-depositional contaminations with Ar^+ sputter using a 2 kV accelerating voltage for 30 s. The depth profile analysis was conducted with Ar^+ stepwise sputtering using an accelerating voltage of 2 kV and an etching area of 1 mm × 1 mm. The X-ray induced photoelectron (XPS) data acquisition area was chosen to be 100 μm × 100 μm in order to increase the accuracy in the depth profiling. All binding energies of Pt, Zr, Ti and O were referenced to Au $4_{f7/2}$ at 84.0 eV. During measurements, the analysis chamber pressure was maintained at $\sim 10^{-11}$ Torr. Finally, the room temperature electrical resistivities of the as-deposited and annealed Pt and composite films were measured using a van der Pauw's four probe technique [44]. The phase analysis and crystallinity of the as-deposited and annealed films were determined by X-ray diffraction (XRD) using a Rigaku Ultima IV powder diffractometer

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