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Platinum thin film electrodes for high-temperature chemical sensor applications

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ABSTRACT

Metal thin film electrodes that may withstand harsh-environments are crucial in the development of advanced chemical sensor applications, as well as, microelectromechanical (MEMS) devices that operate at elevated temperatures. The objective of this work was to investigate high-temperature platinum (Pt) thin films that are compatible for these applications. Special attention was paid to the development of new Pt-based electrode compositions and microstructures that limit sintering and grain coarsening. This work investigated different multilayer coatings of hafnium (Hf) and zirconium (Zr) as both the adhesion layers and grain boundary pinning-phases within the Pt films. All adhesion layers and Pt layers were deposited to the same ~35 nm and ~425 nm thicknesses, respectively. The coating deposition was completed by DC magnetron sputtering on alumina substrates at 200 °C. The multilayer Pt thin films were processed at 800 °C and 1200 °C for 1–48 h, since the anticipated operation temperature is ≥1000 °C. Scanning Electron Microscopy (SEM), Energy-dispersive X-ray Spectroscopy (EDS) and X-ray Photoelectron Spectroscopy (XPS) were utilized to characterize the changes in chemistry and microstructure. Electrical resistivities of the as-deposited and thermally processed Pt films were evaluated by four-point probe technique. The work identified a Hf–Zr–Pt multilayer thin film that demonstrated a room temperature resistivity $<625 \times 10^{-9}\ \Omega$ m after being processed to 1200 °C for 48 h. A lift-off technique was finally used to produce an electrode pattern with the optimum film structure for sustained high-temperature operation.
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1. Introduction

Platinum thin films are used in various microelectronic and micro-sensor applications. The microstructural, chemical, and electrical stability of these films under high-temperature conditions are of major concern. In addition, stability is also a concern for potential extended use in specialized microelectronic applications, especially when the films are used as thin, two-dimensional interconnects or electrodes connecting active components at elevated temperatures. Typical applications of these high-temperature films are aligned with electrodes/interconnects for chemical sensors, micro-heaters and -hotplates within microelectromechanical systems (MEMS) [1–6]. Recently, more advanced MEM systems have been applied within extreme environments, which includes high temperatures and harsh chemical reactants, such as micro-chemical emission sensors, -structural monitoring sensors, -thermocouples, and -fuel cell systems that are utilized at temperatures >600–800 °C [7–13].

High melting point noble metals are most suited for extreme environment applications. Platinum, with its relatively high melting point (1773 °C) and excellent chemical inertness, has long been utilized for MEMs devices capable of operating at elevated temperatures. Pt and other noble metals have a great chemical inertness; however, these metals show poor adhesion and high surface tension toward oxide surfaces. Budhani et al. demonstrated an interface modification between thermally grown aluminum oxide (Al_2O_3) and thin Pt films via reactive sputtering with low levels of oxygen in order to obtain a 20–30 nm Pt_xO_{1-x} layer prior to pure platinum metal deposition. Adhesion tests showed a higher level of adhesion compared to the conventional $Pt + Al_2O_3$ couple. The authors indicated that strong Pt_xO_{1-x} to Al_2O_3 bonding and interdiffusion at the interface were responsible for the enhanced adhesion [14].

Although the controlled oxidation of a sub-layer of Pt showed promise for enhanced wetting and adhesion to oxide substrates, various researchers have focused on incorporating alternative metal/metal oxide layer compositions. These thin coatings were deposited to improve noble metal adhesion, as well as, to improve the thermal stability over prolonged exposure to high temperatures. High temperature operating conditions lead to the development of many structural defects, such as hillocks, film delamination, surface cracking, voids and grain coarsening, which all eventually result in non-uniform film morphology and variable electrical response [1–5,15–18]. At high temperatures (≥700 °C), grain coarsening and hillock formation are the major mechanisms that break the percolated granular network across the polycrystalline film [3,19–22]. Since low-temperature sputtering and evaporation techniques typically produce films with high

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surface area granular structures, these films possess an extremely high driving force for sintering and grain growth processes. High-temperature operation permits the required diffusional kinetics for accelerated grain growth, resulting in the coalescence of the grains and the formation of a poorly percolated structure [21,23]. In other words, the total interfacial and surface energy of the thin film can be minimized by reducing ceramic–metal contact area by creating islands of Pt material. The destruction of the integrity of the continuous film eventually results in complete loss of electrical continuity, which diminishes the functionality, reliability and sensitivity of the micromachined devices.

Metals such as Ti and Ta have been proposed and demonstrated with variable success to decrease both Pt grain coarsening and hillock formation. Lee et al. optimized the procedure first defined by Budhani et al. for deposition of Pt over insulating oxide layers with improved adhesion. According to this procedure, platinum deposition under an oxidation atmosphere, followed by inert atmosphere deposition of Pt and subsequent annealing of silicon substrate at 400–1300 °C, removed the remaining O_2 in the Pt film [24]. Recently, Tiggelaar et al. compared the use of the Pt_xO_{1-x} adhesion layer to the use of Ti or Ta adhesion layers. These layers were deposited by sputtering onto silicon and Si_3N_4 substrates. After annealing between 400 and 950 °C under inert and oxygen containing atmospheres, their electrical and structural performances were characterized [25]. The authors concluded that the operational reliability of Pt films with Ti and Ta adhesion layers are limited to temperatures below 650 °C and 850 °C, respectively. In the same study, the fast diffusion behavior of Ti and the resultant changes to the wetting characteristics of Pt on the Ti layer over different ceramic layers (Al_2O_3, Ta_2O_5, SiO_2 and Si_3N_4) were also described. Firebaugh et al. used a similar Ta adhesion strategy on silicon rich silicon nitride. This study states that the adhesion layer migration and coarsening were the major contributors to the Pt film degradation processes. The same group showed that utilizing a thin Ta adhesion layer and a thick Pt top layer with a ceramic capping layer as an oxygen diffusion barrier (Si_3N_4, Al_2O_3) improved the durability of the Pt thin films utilized in microreactors. A significant lifetime increase was reported in the case where a 300 nm Al_2O_3 capping layer was used. Firebaugh et al. showed that also, the use of a thicker Pt films delays the formation of the initial hole defect, as well as, lower the hillock growth rate [3]. In addition, Jeong et al. investigated the effect of Ta capping layers over a thick Pt top coating and reported an increase in the lifetime of the Pt film with an increase in the thickness of the capping layer [5].

A few researchers have recently shown the use of a Zr adhesion layer for Pt thin films which resulted in greater stabilization of the Pt films to oxide surfaces during high-temperature operation. Maeder et al. compared the use of a Zr adhesion layer to that of Ti and Ta adhesion layer over a Pt electrode within a Pb-based ferroelectric thin film structure [26]. The Ti layer showed its inability to restrict microstructural changes and chemical interdiffusion between the active layers and the substrate. The authors demonstrated the superior features of Zr as an adhesion layer, compared to the Ta counterpart, in terms of the lower reactivity toward lead (Pb), as well as, the desirable diffusion and oxidation characteristics. Mardare et al. proposed the use of a Zr adhesion layer for PZT-capacitor electrodes. These authors showed that it is possible to deposit Pt films at lower temperatures with a Zr adhesion layer compared to the Ti counterpart [16]. Howard et al. utilized a similar strategy for thin Pt films for capacitor applications by utilizing Zr or Hf as an adhesion layer; these adhesion layers enhanced Pt bonding through the formation of an intermetallic phase. The authors also indicated that self-limiting nature of these adhesion layers prevented excessive diffusion to the top of the film when the bottom electrode was subjected to high temperature annealing (500–1000 °C) [1]. Cunha et al. also reported improved high temperature stability of Pt thin films on sapphire substrates by utilizing both a Zr adhesion layer and a thin 1.5 nm ZrO_2 layer deposited between multiple Pt films in an alternating fashion to form the complete composite electrode structure. The researchers demonstrated the method of co-sputtering a Pt/10%Rh alloy with Zr (10^{-5} O_2 partial pressure) as the composite electrode, which showed further stability. These works, as well as a few others [4,27–30], showed that alloying or the inclusion of impurities has a significant effect on the grain boundary mobility, which is valid for both thin films and bulk materials.

The sintering and coarsening mechanisms have a significant impact on the high-temperature behavior of sputtered Pt films, as well as, the electrical conductivity of these films. The addition of an intermediate metal thin film layer has been shown to initially improve the adhesion between oxide substrates and noble metal thin films; however, these films have shown significant microstructural alterations when processed at temperatures between 200 and 800 °C. The aim of this study is to better understand the degradation mechanism of sputtered Pt films with common adhesion layers (such as Ti, Ta, and Zr) at temperatures ≥1000 °C. This temperature regime has not been investigated by previous researchers in the area. In addition, the information gained on the microstructural evolution of both the adhesion layer and Pt film (and their interrelation) will be used to develop an efficient strategy to control the overall degradation of the continuous film. The main focus of this work will be to suppress coarsening and hillock formation through the distinct control of the composition and thickness of the adhesion layer, as well as, the control of the interdiffusion and migration of adhesion layer atoms throughout the Pt film. As shown by a few researchers [27–30], the intentional addition of refractory metal-metal oxide secondary precipitates within the Pt grain boundaries can limit the sintering/coarsening mechanism by Zener-pinning. This work will show the utilization of refractory metal Zr, and further investigation of a more durable and less mobile Hf adhesion layer.

2. Experimental

The adhesion layer compositions and Pt electrodes were sputtered on polished Al_2O_3 substrates through a magnetron sputtering technique (CVC 610 DC Magnetron Sputtering Station) at 100 W. Direct current (DC) mode was used with glow discharge of 505, 384, 390, 395 and 388 V for platinum, zirconium, hafnium, titanium and tantalum, respectively. Primary gas (argon) pressure was 50 mTorr for all coatings. All metal depositions were completed with a base pressure of 3×10^{-6} Torr. The sputtering unit is equipped with a 2 in. diameter sputtering target. The platinum thin films were all deposited onto alumina ceramic substrates that were heated to 200 °C by a quartz lamp heater located behind the sample holder. The deposition temperature was elevated to this temperature to improve atomic surface mobility. The temperature was restricted to 200 °C to permit the future use of high-temperature, stable photoresists for patterning electrodes through a lift-off process.

All adhesion layers were deposited to the same ~35 nm thickness, as well as Pt layer with ~425 nm in thickness, in order to retain consistency between each film alteration. Prior to the experiments, processing correlation was completed for each adhesion layer individually in order to insure a consistent thickness. Thicknesses were confirmed with a Tencor Alpha-Step 200 profilometry to an accuracy of ±3 nm and SEM cross-sectional observations. The annealing studies, which mimics the high temperature operation conditions of the Pt coated samples, were completed at 800 °C and 1200 °C in a conventional tube furnace (MTI GSL 1600×). The heating/cooling rates for the isothermal annealing steps were kept constant at 5 °C/min. The annealing time was varied from 1 to 48 h under a N_2 atmosphere (with a background O_2 and H_2O content of 2 ppm

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