Stable Electrodes and Ultrathin Passivation Coatings for High Temperature Sensors in Harsh Environments

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Abstract — **Sensor operation in harsh environments up to 1000°C requires robust packages including stable electrodes and protective coatings. We have developed nanostructured ultra-thin (< 100 nm) Pt-10%Rh / ZrO_2 electrode structures grown by e-beam co-evaporation that operate at temperatures approaching 1000°C. X-ray diffraction (XRD), resistivity, and electron microscopy (EM) studies indicate incorporation of ZrO_2 within the film delays recrystallization, maintaining a stable morphology. We have also developed ultra-thin (< 50 nm) SiAlON passivation coatings that mechanically protect the sensor surfaces, yet allow interaction with the environment. Different SiAlON stoichiometeries were produced by rf magnetron sputtering of Al and Si targets in O_2/N_2/Ar mixtures. The SiAlON films are amorphous and extremely smooth (< 1 nm rms) and remain so even after extended annealing at 1000°C. Our results are applicable to a wide range of high temperature sensor configurations.**

I. INTRODUCTION

Platinum thin film electrodes required for surface acoustic wave sensors and also used for devices such as chemiresistive, chemFET and optical sensors undergo dramatic morphological changes above 700°C due to recrystallization and dewetting effects resulting in loss of electrical continuity and device failure [1,2,3]. The agglomeration of Pt films is exacerbated when devices require the electrode thickness to be less than 100 nm [3]. Electrodes fabricated from Pt-based alloys and other metallic alloys show improved performance. We have previously examined a variety of electrode configurations including Pt, Zr, ZrO_2, Pt/Rh, and Pt/Au films and found them to exhibit improved temperature stability compared to pure Pt [4]. In the work reported here, a nanostructured Pt-10%Rh / ZrO_2 composite film structure has been further developed and characterized that extends the electrode stability to temperatures approaching 1000°C [5].

Film stoichiometry changes and defect creation also rapidly occur at temperatures in the 700-1000°C range, driving a need for passivation coatings for stable long term sensor performance. Typical protective coatings have thicknesses greater than 1 μm [6]. We have extended our work on SiAlON high temperature coating development [7,8] to focus on the ultra-thin film limit (< 50 nm) to apply their beneficial hardness and chemical properties as protective layers on sensor devices. The ultra-thin SiAlON films are amorphous and extremely smooth, even after extended annealing in oxidizing environments, making them ideal ultra-thin passivation layers for high temperature devices.

II. EXPERIMENTAL PROCEDURE

The fabrication of Pt-10%Rh / ZrO_2 thin film electrodes and SiAlON passivation coatings was performed in a versatile multi-chamber ultra-high vacuum system that consists of a molecular beam epitaxy chamber coupled to four different materials characterization chambers [9]. The Pt-10%Rh / ZrO_2 films were deposited to thickness of 100 nm by co-electron beam evaporation of a high purity Pt-10%Rh charge and a Zr metal charge in a background of $5x10^{-6}$ Torr O_2. The deposition rate was on the order of 4.2 nm/min as monitored by a quartz crystal oscillator. Substrates included sapphire, quartz, or langasite covered with a 7.5 nm thick Zr adhesion layer [10], deposited by e-beam evaporation prior to electrode deposition. The SiAlON films were deposited to a thickness of up to 50 nm on top of the Pt-10%Rh / ZrO_2 films by RF magnetron co-sputtering of Al and Si targets in 50% Ar + 50% N_2/O_2 gas mixtures at a nominal rate of 2.4 nm/min. The RF magnetron power on each target and the N_2/O_2 ratio were adjusted to control the specific SiAlON film stoichiometry.

Following deposition, the films were transferred *in vacua* to another vacuum chamber to measure film composition and purity via X-ray photoelectron spectroscopy (XPS). Once the films were exposed to air, they were characterized by high resolution X-ray diffraction (XRD) using θ-2θ scans to probe film crystallographic texture, Scanning Electron Microscopy (SEM) including X-ray Energy Dispersive Spectroscopy (EDS) to measure morphology and composition changes after annealing treatments, Atomic Force Microscopy (AFM) to characterize surface roughness, and 2-point resistivity measurements to monitor electrical changes. All samples were characterized after deposition and also following thermal treatments inside a tube furnace operating in normal laboratory air.

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III. RESULTS AND DISCUSSION

A. *Pt-10%Rh / ZrO_2 Electrodes*

Co-evaporating Pt-10%Rh and Zr in a 5×10^{-6} Torr O_2 atmosphere leads to the incorporation of a dispersed ZrO_2 phase within the electrode film, thereby yielding a dramatic increase in the long term stability of the electrical resistance and morphology. During the film deposition, the Zr flux was adjusted to achieve approximately 8% ZrO_2 content within the film as verified by XPS. The stability of this film structure compared to Pt and Pt-10%Rh films is demonstrated in Fig.1 by film resistance changes as a function of thermal processing at several temperatures in an air tube furnace. The pure Pt film agglomerates and becomes discontinuous at 750°C (Fig.1a). By alloying Pt with 10%Rh, the Pt agglomeration is delayed but the film immediately becomes discontinuous at 1000°C (Fig.1b). It should be noted that this Pt-10%Rh film also reproducibly exhibits a slight drop in resistance near 800°C. The addition of ZrO_2 leads to a nearly stable film resistance at 1000°C, although the film resistance continues to increase slightly with time (Fig.1c).

X-ray diffraction analysis was performed on the Pt-10%Rh and the Pt-10%Rh / ZrO_2 films to investigate the crystallographic changes caused by the annealing treatment. Fig.2 shows XRD θ-2θ scans from the films plotted on a logarithmic intensity scale before and after 16 hours of annealing at 1000°C. The labeled peaks correspond to the (hkl) planes of the Pt or Pt-Rh grains. The results were the same independent of the substrate (quartz, sapphire, langasite); Figs.2a and 2b correspond to quartz and sapphire substrates, respectively.

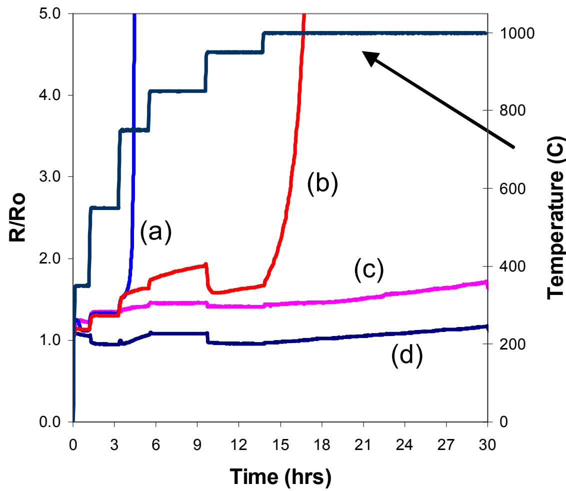

Figure 1. Normalized resistance of 100 nm thick electrode films versus time and temperature (a) pure Pt, (b) Pt/10%Rh alloy, (c) Pt-10%Rh / ZrO_2 alloy, and (d) Pt-10%Rh / ZrO_2 alloy covered with 20 nm SiAlON passivation coating.

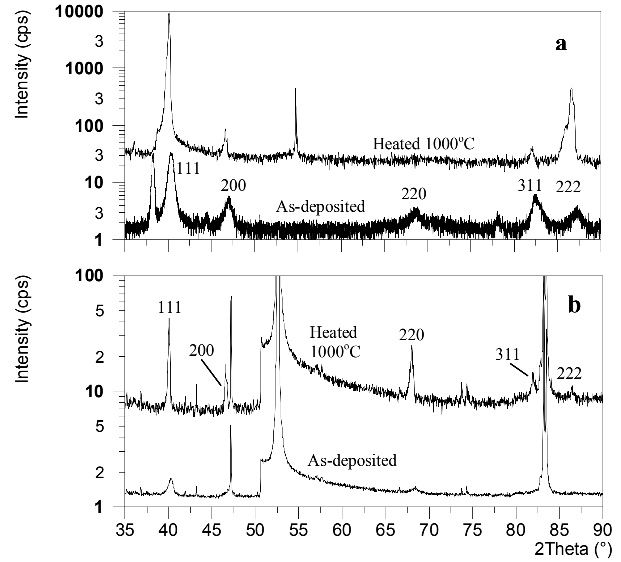

Figure 2. XRD spectra from as-deposited (a) Pt-10%Rh and (b) Pt-10%Rh / ZrO_2 films, and after heating to 1000°C for 16 hours, showing stabilization of a random polycrystalline grain structure by ZrO_2 compared to the recrystalization and growth of (111) oriented grains in the pure Pt-10% Rh film. Unlabeled peaks are from the (a) quartz and (b) sapphire substrates.

The measurements indicate that the Pt-10%Rh films deposited at room temperature have a random polycrystalline texture. Adding ZrO_2 into the film leads to only subtle broadening of the peaks and minimal intensity changes in the as-deposited XRD spectrum, suggesting the formation of a slightly finer grain structure and possibly a slightly more random grain distribution. Heating a Pt-10%Rh film to 1000°C results in the formation of a highly oriented (111) crystallographic texture as evidenced by the very large ratio of the (111) peak intensity to other (hkl) peaks. Along with the increased grain size (narrower peak width), this indicates that the grains re-crystallize and grow with (111) planes parallel to the sample surface. In contrast, for a sample containing co-deposited ZrO_2 the ratio of the (111) peak intensity to other (hkl) peaks only increases modestly following heating to 1000°C (Fig.2b), indicating that there is much less recrystallization and growth of (111) oriented grains and that the polycrystalline texture is largely retained.

No evidence of a crystalline ZrO_2 phase was observed in the as-deposited samples indicating that the ZrO_2 is likely amorphous or extremely fine grained. Following heating to 1000°C, the presence of very broad tetragonal phase ZrO_2 peaks were detected. In some samples, there was also possible evidence of small amounts of rhodium oxide.

Fig.3 shows a secondary electron SEM image with faceted shaped bright crystallites that presumably form during the film recrystallization, which is consistent with the XRD interpretation. EDS analysis of the dark regions

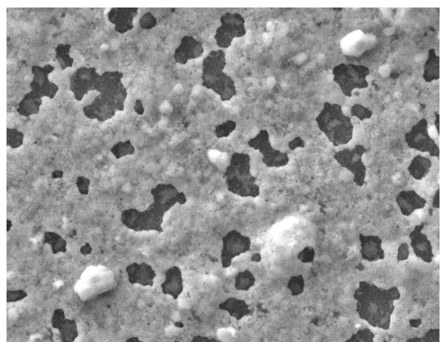

Figure 3. SEM image from an annealed Pt-10%Rh film showing dark regions consisting of just the Zr adhesion layer and brighter Zr, Pt, Rh containing regions made up recrystallized grains. The length bar equals 1 µm.

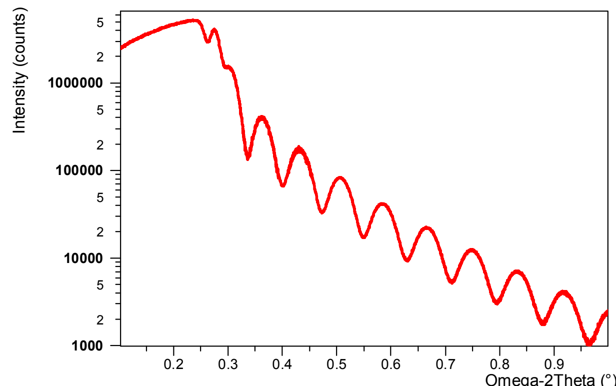

Figure 4. X-ray reflectivity spectrum from a $Si_3Al_3O_3N_5$ film with sharp persistent fringes indicating a film thickness of 49.8 nm and roughness < 1 nm.

indicates only Zr present whereas the lighter regions contain Zr, Pt, and Rh. Long term failure after extended exposure to 1000°C in air (> 100 hours) is caused by the formation of an interconnected network of these dewetted regions that breaks the electrical pathway.

The major effect of the co-deposited ZrO_2 component on the annealed films is to retard the kinetics of the film recrystallization process, thereby preserving a largely random polycrystalline grain structure. Suppression of the recrystallization and growth of (111) oriented grains results in improved electrical continuity at high temperatures. This significant result enables long term high temperature SAW sensor measurements as discussed in a related paper [11].

B. *SiAlON Ultra-thin Passivation Coatings*

Protective layers on sensor devices need to be ultra-thin to achieve low mass loading and allow gas diffusion to the underlying active sensor layers. Based on our previous work in developing $Si_xAl_yO_zN_{1-x-y-z}$ high temperature coatings [5,7,8], we have found that these ultra-thin oxynitride coatings have many attributes that make them attractive as sensor passivation coatings including high hardness, thermal stability, wear resistance, and smoothness.

RF magnetron co-sputtering of Al and Si targets in $Ar/O_2/N_2$ mixtures allows precise control of the specific $Si_xAl_yO_zN_{1-x-y-z}$ stoichiometry. Our work has emphasized oxygen-rich and nitrogen-rich film compositions with nearly equal amounts of Si and Al. The as-deposited SiAlON films are amorphous as determined by XRD and remain so even after extended annealing up to 1500°C in air [7,8]. Furthermore, the films are extremely smooth as measured by AFM and demonstrate hardness greater than sapphire [8]. Fig.4 shows an X-ray reflectivity spectrum acquired from a 50 nm thick $Si_3Al_3O_3N_5$ film showing sharp multiple oscillations that persist over a large range of incident angles. Analysis of this spectrum indicates that the amorphous SiAlON layer is very homogeneous with a thickness of 49.8 nm, has a nominal density of 3.2 g/cm^3, and is extremely smooth (< 1 nm rms).

A 20 nm thick SiAlON layer is effective in protecting a Pt-10%Rh / ZrO_2 film during annealing at 1000°C for 16 hours as shown in Fig.1d. The passivation of the electrode surface further retards the film recrystallization process and provides longer stability at 1000°C. This improvement is also readily visible in the SEM images shown in Fig.5. As in Fig.3, the dark regions are areas where no Pt-Rh EDS signal is present. The film morphology becomes rougher as the Pt-Rh grains recrystallize and mass transport occurs from the dark regions into the growing Pt-Rh grains. Clearly the SiAlON layer acts to retard the recrystallization process.

The SiAlON films were analyzed by XPS following the air annealing treatments and it was found that the films lose nitrogen. The surface oxidation leads to the formation of an amorphous aluminum silicate layer that also serves to passivate the surface. We are currently carrying out further studies to investigate the kinetics of the SiAlON oxidation behavior.

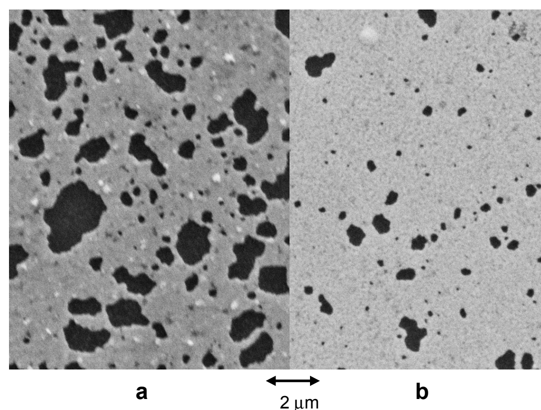

Figure 5. Scanning electron micrograph showing morphological changes following a 16 hr anneal at 1000°C on a Pt-10%Rh electrode film. (a) without and (b) with a 20 nm SiAlON passivation coating present.

IV. CONCLUSIONS

Adding a dispersed ZrO_2 component into Pt-10%Rh thin films retards film recrystallization, agglomeration, and dewetting at temperatures in the 700-1000°C range. This stabilization of metal electrodes is especially important in sensor applications requiring electrode thicknesses less than 100 nm, such as surface acoustic wave sensors. An ultra-thin (< 50 nm) SiAlON passivation layer further slows down morphological changes in the electrodes and has an additional benefit of providing a hard, wear resistant, smooth protective layer on the sensor surface. These materials are useful for a variety of high temperature sensor applications.

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