Influence of composition and multilayer architecture on electrical conductivity of high temperature Pt-alloy films

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Abstract: A multilayer film architecture has been investigated as a means to stabilize the morphology and electrical conductivity of Pt-based nanocomposite films that are exposed to temperatures up to 1200°C in air. The multilayer architecture consists of a 150 nm thick conducting Pt-alloy electrode inserted between a 10 nm thick adhesion layer and a 50 nm thick protective capping layer on sapphire or langasite substrates. The Pt-alloy **films** were fabricated by e-beam co-evaporation of a Pt or Pt₈₃Rh₁₇ source and a range of different alloying elements (Co, Ni, Cr, Rh, Ta, Ti, Nb, Al, Sn) or oxides (HfO₂, ZrO₂, Nb₂O₃, Y₂O₃, RuO₂, CeO₂, NiO, CoO, MnO₂). Second phase inclusions or interlayers within the Pt-alloy films provide grain boundary pinning and hinder agglomeration of Pt grains, resulting in films that retain conductivities > 1x10⁶ S/m after annealing in air. Pt-Al₂O₃, Pt-HfO₂, and nanolaminate Pt-Ni/Pt-Zr films performed the best, remaining conductive after annealing to 1050-1150°C. For Pt-Rh/HfO₂ films, adhesion layers of Ni, Zr, Y, and CeO_x yielded the highest film stability temperature. Capping layers of ZrO₂ or Y₂O₃ did not significantly improve the film stability. Electrically conducting **films** that remain stable above 1000°C in oxidizing high temperature environments have potential applications **as electrodes** in a wide range of technologies, including microwave acoustic sensors, MEMS devices, and fuel cells.

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1. INTRODUCTION

Many technologies require thin film electrodes that can either operate or be processed at high temperatures (500-1200°C). Examples include wireless microwave acoustic harsh environment temperature sensors [1,2], gate electrodes for advanced CMOS devices [3,4], SiC electronics [5,6], MEMS micro-thrusters [7] micro-reactors [8,9], micro-hotplates [10–12], thin film anemometers [13,14], thin film thermocouples [15], thin film solid oxide fuel cell devices [16,17], and micro light sources for IR chemical analysis systems [18,19]. Although thick film materials can be used at these temperatures, in most applications the film thickness cannot exceed a few hundred nanometers and stable thin film materials are lacking. Strategies to stabilize thick (~few to 100 μm) films, such as the use of protective scale layers, are not successful when applied to thinner films. Furthermore, when heated to high temperature, thin metallic films tend to agglomerate into isolated islands or undergo oxidation reactions, which lead to insulating behavior and device failure. Other failure modes include evaporation of the film itself or film oxidation and evaporation of volatile oxides. Thus, identification of thin film materials that can maintain high electrical conductivity, particularly above 1000°C in the presence of oxygen, remains a challenge.

In previous work [1,20–23], it has been shown that two different strategies for manipulating the structure of Pt-based thin film electrodes can extend their operating range up to near 1000°C. In one method, shown in Figure 1(a), the Pt-alloy electrode layer is deposited with a second phase material, such as ZrO_2 , which provides grain boundary pinning and stabilization of a connected network of conducting Pt grains. In a second method, Figure 1(b), thin nanolaminate interlayers such as Zr, ZrO_2 , HfO_2 , or ZrB_2 are used to break up the structure of the electrode layer and retard agglomeration.

In addition to the nanostructured electrode film, an adhesion layer is required to avoid delamination of the electrode layer from the substrate. Effective adhesion layers are typically

formed by using a metal with high reactivity that forms a chemical bond with the insulating substrate (usually a metal oxide) and forms a strong metal-metal (alloy) bond with Pt alloys, as well as forms stable oxides when heated in air at high temperatures. This layer can also provide other benefits, such as reducing film stress by mediating the coefficient of thermal expansion (CTE) mismatch between the substrate and electrode material. The adhesion layer can influence the interfacial energy at the buried electrode interface, thus modifying the agglomeration behavior. In the absence of an additional interfacial barrier layer, the adhesion layer can also act to retard diffusion of substrate atoms into the electrode layer.

Further measures that can be taken to improve high temperature film performance include the addition of an interfacial barrier layer and a capping layer [22–24]. The interfacial layer can reduce degradation of the electrode layer caused by interdiffusion effects and reaction with the substrate. In experiments that highlighted the importance of the interfacial layer, the same electrode layer was grown on different substrates and then furnace tested to failure [22]. Films grown on stable oxide substrates such as sapphire and quartz remain conductive to higher temperatures than films grown on langasite (LGS - $\text{La}_3\text{Ga}_5\text{SiO}_{14}$) and langatate (LGT - $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$) crystals. The results also showed that an Al_2O_3 interfacial layer grown by an ALD process helps reduce interdiffusion and reaction at the electrode-substrate interface at high temperature. In addition, the use of a capping layer can alter the free energy balance that drives the agglomeration process, impede high temperature electrode oxidation in air, and provide mechanical protection. Both SiAlON and Al_2O_3 capping layers have been shown to increase the maximum temperature at which electrode films remain conducting and morphologically stable, although Al_2O_3 layers have been shown to be more effective [22–24].

In this paper, results of annealing experiments are reported for a large number of prospective nanocomposite thin film materials that embed either pinning inclusions or pinning interlayers into a Pt-alloy conducting electrode nanostructure. Several thin film materials are

investigated up to 1200°C in air for use as the Pt-alloy conducting electrode, the pinning additive in the electrode layer, the adhesion layer, and the protective capping layer.

2. EXPERIMENTAL

Platinum-alloy films were deposited onto 0.5 mm thick epitaxially polished langasite ($\text{La}_3\text{Ga}_5\text{SiO}_{14}$) or r-sapphire ($\alpha\text{-Al}_2\text{O}_3$) wafers having < 2 nm rms roughness. The depositions were carried out at room temperature in an ultra-high vacuum chamber with typical base pressure $< 10^{-7}$ Pa. The thin film materials were deposited using electron-beam evaporation of $\geq 99.9\%$ purity metal sources (Pt, Mn, Ni, CeO_x , Zr, Nb, Cr, Hf, Y, Ti, Ta, Al, Sn, Ru, Co) either in vacuum ($\sim 1 \times 10^{-7}$ Pa) or in 5.0 grade O_2 gas ($\sim 2.7 \times 10^{-3}$ Pa), depending on whether a Pt-metal or Pt-metal oxide film composition was grown. Since the total oxygen content in the films depended on the reactivity of the particular metals used, only the nominal Pt and metal content (atomic %) is reported for films deposited in the presence of O_2 gas. Pt-Rh films were deposited by e-beam evaporating a Pt90%-Rh10% by weight alloy charge, which corresponds to a $\text{Pt}_{83}\text{Rh}_{17}$ alloy composition using atomic % as quoted for the other alloys in this study. All the other Pt-alloys were formed via co-evaporation from single element sources. The deposition chamber was equipped with two four-pocket e-beam evaporators, which enabled co-deposition of two materials and also facilitated changing of deposition material without breaking vacuum when growing multi-layered structures.

Quartz crystal deposition rate monitors (QCMs) were located both at the sample plane and in positions near the e-beam sources to monitor them independently. Tooling factors were determined by depositing single element films and comparing QCM thicknesses at each location. Film densities for each alloy material were determined by using the measured tooling factor to deposit nominally 50 nm thick films onto polished fused silica substrates with a shadow mask defining a 0.25 mm stripe, and measuring the stripe thickness with a stylus profilometer. Tabulated values of the Z-ratio for the QCMs were used for all depositions. For co-deposited

materials, film composition and thickness were controlled by adjusting the e-beam power levels, based on rate measurements using each respective QCM head with the appropriate calibrated tooling and density values. In situ XPS analysis was also used to verify the average as-deposited film compositions. The adhesion layers were deposited onto the sapphire or langasite substrates via e-beam evaporation to a nominal thickness of 10 nm, and subsequent electrode layers were immediately deposited to their desired thickness, which were typically within $\pm 10\%$ of their targeted value of 150 nm, as measured by stylus profilometry. Capping layers of 50 nm thickness were deposited by e-beam evaporation in the presence of 2.7×10^{-3} Pa O_2 .

Following film deposition, samples were diced to dimensions of 3 mm x 6.5 mm for furnace heating and conductivity measurements. The large number of candidate electrode materials explored in this study was screened by determining the maximum temperature to which blanket-deposited thin films remained electrically conductive. At temperatures above 800°C, rapid solid state diffusion can induce compositional changes near the interface between a bond wire and a film, which can lead to bond deterioration and loss of electrical connection as well as changes in the properties of the neighboring electrode film [25]. In order to efficiently and accurately screen large numbers of samples at temperatures up to 1200°C, an alternative non-wire bonding method was employed in which multiple blanket deposited samples were simultaneously heated within a tube furnace at 800, 900, 1000, 1050, 1100, 1150, and 1200°C by precisely positioning them on a sample fixture that spanned the temperature gradient within the tube furnace. All annealing treatments were the same, and consisted of a 10°C/s ramp from 25°C to the desired temperature for a 4 hour hold, followed by cooling to room temperature. Following this heating cycle, 4-point conductivity measurements were made at room temperature on all samples and selected samples were imaged using a Zeiss NVision 40 cross beam FIB/SEM instrument. To screen the large number of film configurations, room temperature 4-point conductivity

measurements were compared since these values are a function of the high temperature film nanostructure and are a good measure of relative film stability. Using this method, up to four different types of blanket film samples were evaluated over the range 800-1200°C during one experimental run with no danger of artifacts due to bonding of connecting wires.

3. RESULTS AND DISCUSSION

3.1 Adhesion Layer Studies

Seven different materials (Mn, CeO_x, Ni, Cr, Nb, Hf, Y) were identified and tested as the 10 nm adhesion layer under a 150 nm thick Pt₈₃Rh₁₇/HfO₂ electrode film, and compared to the performance of the same Pt₈₃Rh₁₇/HfO₂ film but with a Zr adhesion layer as reported previously [23]. Mn, Ni, and CeO_x were tested on sapphire substrates, and Cr, Nb, Hf, and Y tested on langasite substrates. Figure 2 shows conductivity results for Pt₈₃Rh₁₇/HfO₂ films after annealing for 4 hours in air at each temperature. Films with adhesion layers of Cr or Nb on langasite, and Mn on sapphire, failed at a 50°C lower temperature than films with Zr adhesion layers, whereas films with Hf, Y, or CeO_x adhesion layers maintained conductivity to the same temperature. Compared to films with Zr adhesion layers, following heating to 1050°C, films with Hf had lower conductivity, films with Y had nearly the same conductivity and films with CeO_x had somewhat higher conductivity. In all cases, the adhesion layer became oxidized during the high temperature annealing, and the failure temperature correlates with different degrees of agglomeration caused by each adhesion layer material. Overall, the best performing adhesion layer was Ni, which on a sapphire substrate yielded a Pt₈₃Rh₁₇/HfO₂ film that remained conductive after heating to 1100°C, which is 50°C higher than for any other adhesion layer.

3.2 Platinum Alloy Studies

Pt-Rh alloy thin films have been demonstrated to have superior stability compared to pure Pt and Pt-Au alloy films [20]. In this section, high temperature testing results are reported for a number of other Pt-alloy films. It has been reported that the high temperature oxidation of bulk

Pt-alloys with small additions of Ti, Nb, and Ta produce weight gain during heating in air at 1300°C due to oxidation [26]. As most alloys lose weight at these temperatures due to loss of volatile platinum oxide, these alloys were considered as good candidates for the thin film Pt-alloy electrodes. In addition, both Ta and Nb have melting points significantly higher than Rh. The atomic percentage of the second component that was incorporated into these films followed those suggested in the literature: 6% Ti, 4% Ta, and 15% Nb. Cobalt is used as a grain refiner in bulk platinum alloys suggesting that Co additions could slow agglomeration in alloy films by inhibiting grain growth. Platinum aluminides are used for corrosion resistant coatings and alumina is a very stable high temperature ceramic. Other elements were chosen based on their use in high temperature alloys, high melting points or presence of stable oxides.

The Pt-alloy films were grown by co-depositing Pt with: Ti, Ta, Nb, Al, Ru, Sn on langasite substrates, and Co, Cr, Ni, Si on sapphire substrates; in all cases, a Zr adhesion layer was used. Figure 3 shows the results of conductivity measurements following 4 hour annealing treatments in air, along with data for a pure Pt and Pt₈₃Rh₁₇ film for reference. The Pt₅₀Si₅₀ and Pt₈₃Ru₁₇ films failed after initially heating to 800°C and are not shown in the figures. The Pt₈₆Al₁₄ film was the best film and remained conductive to 1100°C on langasite. The Pt₈₅Nb₁₅, Pt₈₀Sn₂₀, and Pt₈₅Co₁₅ alloy films show promise, having survived to temperatures equal to or higher than the reference Pt₈₃Rh₁₇ film. The Pt₈₅Co₁₅ and Pt₉₀Ni₁₀ alloys deposited on sapphire had the same maximum survival temperature as Pt₈₃Rh₁₇ on langasite, with the additional benefit of higher conductivity. Increasing the Ni content up to Pt₇₀Ni₃₀ extended the film operational temperature range, although film conductivity was reduced by about a factor of two. Films that did not perform as well as the reference Pt₈₃Rh₁₇ film, failing after heating at 900°C, included Pt₉₀Cr₁₀, Pt₉₄Ti₆ and Pt₉₆Ta₄ as well as the pure Pt film.

Secondary electron images that elucidate the differences in film morphology of the Pt₈₅Nb₁₅, Pt₈₃Rh₁₇, and Pt₉₆Ta₄ films after annealing in air for 4 hours at 1000°C are shown in

Figure 4. The films have agglomerated to different degrees, with the $\text{Pt}_{85}\text{Nb}_{15}$ film having the smallest interconnected Pt-rich grain network. Both the $\text{Pt}_{83}\text{Rh}_{17}$ and $\text{Pt}_{96}\text{Ta}_4$ films show isolated agglomerated grains, with the highest degree of agglomeration for $\text{Pt}_{96}\text{Ta}_4$, consistent with the electrical characterization results.

Since the $\text{Pt}_{86}\text{Al}_{14}$ film out-performed the other alloy films tested in Figure 3, additional Pt-Al films were grown to determine the effect of varying the Al content and also study the influence of introducing O_2 in the deposition chamber to form oxide or sub-oxide phases during growth. Figure 5 shows conductivity results for a series of Pt-Al alloy film compositions grown on sapphire substrates with a Zr adhesion layer. The films designated $\text{Pt-Al}_2\text{O}_3$ were grown in 2.7×10^{-3} Pa O_2 , whereas those designated Pt-Al were grown in ultra-high vacuum. The best performance was obtained from the $\text{Pt}_{86}\text{-Al}$, $\text{Pt}_{86}\text{-Al}_2\text{O}_3$, and $\text{Pt}_{72}\text{-Al}_2\text{O}_3$ films, which remained conductive upon heating to 1150°C for 4 hours. The fact that the $\text{Pt}_{86}\text{-Al}$ and $\text{Pt}_{86}\text{-Al}_2\text{O}_3$ gave very similar results gives evidence that the metallic Al and Al sub-oxide components in the films become fully oxidized during high temperature air oxidation, yielding the same film nanostructure of Al_2O_3 pinning inclusions that stabilize the Pt grains. Films with higher Pt content (93%) only maintained conductivity to 1050°C , indicating that the Al content of these films was too low to effectively hinder Pt agglomeration.

To observe possible substrate effects, a $\text{Pt}_{86}\text{Al}_{14}$ film was grown on a langasite substrate and both $\text{Pt}_{86}\text{-Al}$ and $\text{Pt}_{86}\text{-Al}_2\text{O}_3$ films were grown on a langasite substrate coated with a 50 nm thick Al_2O_3 interfacial barrier grown in an atomic layer deposition (ALD) reactor; all samples included a Zr adhesion layer and the two $\text{Pt}_{86}\text{-Al}$ electrode films were grown in the same deposition run. Up to 1000°C , the $\text{Pt}_{86}\text{-Al}$ film grown on ALD Al_2O_3 had values of conductivity very close to the $\text{Pt}_{86}\text{-Al}$ film without the ALD Al_2O_3 layer. Above 1000°C , the film with the extra interfacial layer maintained higher conductivity than the sample without the interfacial Al_2O_3 layer, but both failed at the same temperature of 1150°C . The $\text{Pt}_{86}\text{-Al}_2\text{O}_3$ film grown on

Al₂O₃-coated langasite performed very similarly to films of the same composition grown on sapphire substrates, and also similar to the Pt₈₆-Al₁₄ film grown on ALD Al₂O₃, which did not fail until heating to 1150°C. These results suggest that the langasite substrate does not significantly increase film degradation at lower temperatures, and that the ALD Al₂O₃ interfacial barrier layer is beneficial when heating samples above 1000°C.

Figure 6 shows SEM images that illustrate the influence of varying the Pt-Al₂O₃ composition on the film nanostructure. Following heating to 1050°C, the Pt₉₃-Al₂O₃ film with the lowest Al₂O₃ content has agglomerated into isolated islands as shown in Figure 6(a), consistent with zero film conductivity at this temperature. There is evidently an insufficient amount of Al₂O₃ present to induce grain boundary drag and hence prevent agglomeration. After heating films with higher Al₂O₃ content (Pt₈₆-Al₂O₃ and Pt₇₂-Al₂O₃) to 1100°C, holes form in the conducting Pt-alloy phase due to areas of dewetting, as shown in Figures 6(b) and 6(c), but both films remain continuous. The Pt₇₂-Al₂O₃ film (Fig. 6c) shows evidence of a two-phase mixture, possibly due to excess Al₂O₃ on the surface. Of particular significance is the absence of any large Pt grains in these films following heating to 1100°C. In contrast, most other Pt and Pt-Rh alloy films heated above 1000°C undergo considerable Pt grain growth and recrystallization resulting in large crystalline grains.

3.3 Pinning Material Studies

The effect of using different types of metal oxide inclusions for grain boundary pinning and high temperature stabilization of Pt₈₃Rh₁₇ films was studied. Previous work has shown that incorporating ZrO₂ into Pt₈₃Rh₁₇ films at levels corresponding to 10 – 28 atomic % Zr as determined by XPS, can extend the conducting range of Pt₈₃Rh₁₇ films up to 1000°C via formation of ZrO₂ inclusions that help stabilize the film morphology [24]. Based on these results, a ratio of the pinning metal concentration to Pt concentration of 27% was targeted in the present work. Figure 7(a) shows the conductivity results for seven prospective pinning materials: MnO₂,

CeO₂, NiO, HfO₂, CoO, Al, and ZrC added to Pt₈₃Rh₁₇ films on sapphire substrates. In addition, four prospective oxide pinning materials: HfO₂, Y₂O₃, Nb₂O₃, and RuO₂ were tested on langasite substrates and compared to ZrO₂, Zr, and no pinning phases after annealing up to 1200°C as shown in Figure 7(b). Except for ZrC, Zr, and Al, the films were grown in a 2.7x10⁻³ Pa background of O₂ to create oxide pinning phases during the deposition; subsequent air annealing caused the pinning metal components in all the films to reach their maximal valence oxide state.

On sapphire substrates, HfO₂ proved to be the best pinning additive, with the film remaining conductive up to 1150°C, which is 50°C higher than the same film on a langasite substrate. Films with Al and MnO₂ failed at a 50°C lower temperature than the film with HfO₂, with performance similar to films with ZrO₂ as a pinning additive. Interestingly, the Pt₈₃Rh₁₇-Al film in these tests did not perform as well as the Pt/Al₂O₃ films discussed in Section 3.2. The presence of Rh is evidently associated with the earlier failure of the Pt₈₃Rh₁₇-Al film. The film with CeO₂ as an additive failed after heating at 1050°C, and films with ZrC, CoO and NiO inclusions did not perform as well, failing after heating at 1000°C. Although carbides are attractive due to their high temperature performance and alternate chemistry as opposed to oxides, the sample with ZrC as a pinning material was only conductive to 900°C, possibly due to oxidation of the ZrC phase at higher temperatures.

On langasite substrates, the Pt₈₃Rh₁₇ film with no pinning additives, labeled ‘None’ in Figure 7(b), was conductive after heating to 900°C and failed after heating to 1000°C, whereas the Pt₈₃Rh₁₇-ZrO₂ reference material remained conductive after heating to 1000°C and failed after heating at 1050°C, consistent with previous work [23]. Co-deposition of Zr in the absence of oxygen resulted in a film that performed very similar to a film co-deposited with Zr in a 2.7x10⁻³ Pa O₂ background pressure, again signifying that inclusions of the maximum valence oxide, ZrO₂, are formed during the high temperature air anneal. Results from other films deposited on langasite substrates indicate that (i) films with Nb₂O₃ and RuO₂ are inferior compared to samples

containing ZrO_2 , (ii) films with Y_2O_3 have a similar failure temperature and somewhat higher conductivity, and (iii) films with HfO_2 have a higher survival temperature by approximately 50°C . Replacement of Zr by Ru caused the film to fail at 1000°C , likely due to the higher vapor pressure of RuO_2 . Niobium has atomic number that is one larger than Zr and a higher melting point, but use of Nb_2O_3 as a pinning material also resulted in failure at 1000°C . Yttrium has an atomic number one lower than Zr, and Y_2O_3 has been used for pinning in bulk Pt-based materials and phase stabilization of zirconia. Use of Y_2O_3 resulted in higher conductivity at 900°C and 1000°C , but did not extend the survivability to higher temperatures. Hafnium has very similar chemical properties to Zr, but twice the mass and hence lower atomic mobility. The replacement of Zr with Hf resulted in increased film conductivity at 900°C and 1000°C and a 50°C increase in the maximum temperature at which the film remained conducting.

Experiments were performed to determine if adding a grain boundary pinning mechanism to Pt-Co and Pt-Ni films would extend their operational temperature range. Because the deposition system can only co-evaporate two materials at a time, the film architecture of Figure 1(b) was used. Thin, 7.5 nm interlayers of Pt co-deposited with Zr were interleaved with 27.5 nm thick layers of co-evaporated Pt-Co or Pt-Ni, for a total stack of 8 layers grown on sapphire substrates. A Pt-Co or Pt-Ni layer was deposited directly over the Zr adhesion layer and the stack was terminated with Pt-Zr as the top layer. The conductivity results after furnace testing of these two film types are shown in Figure 8. The $\text{Pt}_{85}\text{Co}_{15}/\text{Pt}_{84}\text{Zr}_{16}$ nanolaminate film with a 11:3 layer ratio remained conductive after heating to 1100°C and the $\text{Pt}_{90}\text{Ni}_{10}/\text{Pt}_{84}\text{Zr}_{16}$ nanolaminate film survived to 1150°C .

Additional Pt-Ni and Pt-Co nanolaminate films were grown to explore the effect of changing the interlayer thickness ratio and the Pt-Ni composition ratio. A $\text{Pt}_{70}\text{Ni}_{30}/\text{Pt}_{84}\text{Zr}_{16}$ nanolaminate film with a 1:1 interlayer ratio and 17.5 nm nominal layer thickness performed in a

nearly identical manner as a film with a 11:3 thickness ratio and Pt₉₀Ni₁₀ composition. The Pt₇₀Ni₃₀ film was expected to outperform the Pt₉₀Ni₁₀ film given the results shown in Figure 3, but the nearly equivalent performance suggests that a 1:1 interlayer ratio is less effective. Figure 8 also shows the effect of adding O₂ to the growth chamber for a similar 1:1 thickness ratio film (+). The creation of Ni-oxides in the as-deposited film was highly detrimental, in contrast to Pt-Al₂O₃ films where the addition of O₂ was found to improve the film operational temperature and film reproducibility. Not shown in Figure 8 is a Pt-Ni-based film with Pt-Al pinning layers deposited in the same manner as described above. Testing indicated the Pt-Al interlayers do not work as well as Pt-Zr interlayers with Pt-Ni-based films. Figure 8 also shows the effect of adding an ALD Al₂O₃ capping layer, as discussed in the next section.

SEM imaging of the Pt-Ni and Pt-Co nanolaminate films after heating at 1100°C (Figure 9) shows very similar morphology, with larger Pt crystallites appearing in the Co containing film. Based on the Z-contrast in the backscattered electron images as well as EDS analysis, the bright areas are Pt-rich with no detected Ni or Co, the small dark regions are ZrO₂ precipitates, and the dewetted regions contain primarily Ni or Co atoms.

3.4 Capping Layer Studies

Capping layers are useful for mechanically protecting the underlying electrode film and also for potentially extending the operating temperature range by retarding film agglomeration and acting as a diffusion barrier to isolate the electrode film from oxygen or other reactive gases. Capping layer studies were performed on Pt₈₃Rh₁₇-ZrO₂ electrode films by investigating the effects of adding a nominally 50 nm thick Y₂O₃ or ZrO₂ capping layer. In both cases, the additional capping layer resulted in improved conductivity after heating to 1000°C, with the Y₂O₃ capping layer showing the better performance. After heating to 1050°C for 4 hours, both the uncapped and ZrO₂ capped films were no longer conductive while the Y₂O₃ capped film exhibited very low but non-zero conductivity. As previously reported [23], depositing an Al₂O₃

capping layer via ALD onto a $\text{Pt}_{83}\text{Rh}_{17}\text{-HfO}_2$ film increases film conductivity following annealing to 1100°C by nearly a factor of five, although the films still fail when heated above 1100°C . The effect of adding 50 nm thick ALD Al_2O_3 capping layers onto $\text{Pt}_{90}\text{Ni}_{10}/\text{Pt}_{84}\text{Zr}_{16}$ and $\text{Pt}_{85}\text{Co}_{15}/\text{Pt}_{84}\text{Zr}_{16}$ nanolaminate films is shown in Figure 8. Addition of the Al_2O_3 cap resulted in decreased conductivity for the Pt-Co/Pt-Zr nanolaminate film above 1000°C , whereas the conductivity of a Pt-Ni/Pt-Zr nanolaminate film was significantly improved with the addition of the cap.

4. CONCLUSIONS

Metallic conducting electrode films tend to either agglomerate into isolated islands or become heavily oxidized at high temperature in air leading to insulating behavior. In this work, a wide range of 150 nm thick Pt-alloy films containing a dispersed oxide phase (TiO_2 , Ta_2O_5 , Nb_2O_3 , Al_2O_3 , RuO_2 , SnO_2 , CoO , Cr_2O_3 , NiO , SiO_2 , ZrO_2 , Y_2O_3 , HfO_2 , CeO_2 , MnO_2) were screened for their electrical conductivity after annealing up to 1200°C in air. The films were deposited onto sapphire and langasite substrates coated with a 10 nm thick adhesion layer (Cr, Nb, Hf, Y, Mn, Ni, CeO_x) using e-beam co-evaporation in both vacuum and in background O_2 gas. Following air heat treatments up to 1200°C , all the metallic components completely oxidized into a second phase oxide that coexist with Pt-rich grains. Layering or adding oxide inclusions provides grain boundary pinning and hinders the agglomeration process to achieve electrical and morphological film stabilization. The best performing electrode films that were tested in this study were Pt- Al_2O_3 , Pt- HfO_2 , and Pt-Ni/Pt-Zr nanolaminate films, which retained conductivity after heating in the $1050\text{-}1150^\circ\text{C}$ range.

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FIGURE CAPTIONS

- Fig. 1** Possible multi-layer film architectures for realizing conducting thin film electrodes that remain stable above 1000°C in air. The nanocomposite films can be designed to have either (a) phase inclusions or (b) interlayer phases to pin grain boundary motion at high temperature.
- Fig. 2** Room temperature electrical conductivity of Pt₈₃Rh₁₇-HfO₂ electrode films with different 10 nm thick adhesion layers deposited on (a) sapphire and (b) langasite substrates, after heating in air for 4 h at the indicated temperatures.
- Fig. 3** Room temperature electrical conductivity of various Pt-alloy electrode films on (a) sapphire and (b) langasite substrates after heating in air for 4 h at the indicated temperatures. The electrode films were 150 nm thick with a 10 nm Zr adhesion layer, and alloy compositions are given in atomic percent.
- Fig. 4** Secondary electron images of (a) Pt₈₅Nb₁₅ (b) Pt₈₃Rh₁₇ (c) Pt₉₆Ta₄ films with a Zr adhesion layer on langasite substrates after heating in air for 4 h at 1000°C.
- Fig. 5** Electrical conductivity of Pt-Al films (black lines) and Pt-Al₂O₃ films (red dotted lines) after heating in air for 4 h at the indicated temperatures. The solid data markers denote different Pt content, and the open data markers denote a second film with the same nominal composition as the film with the solid marker.
- Fig. 6** Secondary electron images of (a) Pt₉₃-Al₂O₃ film heated in air to 1050°C; (b) Pt₈₆-Al₂O₃ film heated in air to 1100°C; and (c) Pt₇₂-Al₂O₃ film heated in air to 1100°C.
- Fig. 7** Electrical conductivity of Pt₈₃Rh₁₇ films co-deposited with different grain boundary pinning materials after heating for 4 h in air at the indicated temperatures: (a) on sapphire substrates with Zr adhesion layer, and (b) on langasite substrates with Zr adhesion layer.
- Fig. 8** Electrical conductivity of Pt-Ni and Pt-Co electrode films containing Pt₈₄Zr₁₆ pinning interlayers on sapphire substrates with Zr adhesion layer after heating for 4 hours in air at the indicated temperatures. Also shown is a Pt₉₀Ni₁₀ film with ZrO_x interlayers.
- Fig. 9** Secondary electron (left) and backscattered (right) images from (a) [Pt₈₅Co₁₅/Pt₈₄Zr₁₆]_{x4} and (b) [Pt₉₀Ni₁₀/Pt₈₄Zr₁₆]_{x4} multilayer films after heating in air for 4 h at 1100°C.
- Fig. 10** Electrical conductivity of Pt₈₃Rh₁₇-ZrO₂ films on langasite substrates with Zr adhesion layer and different capping layers after heating in air for 4 h at the indicated temperatures.

Figure 1 revised
capping layer

electrode with
pinning
INCLUSIONS

adhesion layer

interfacial barrier

substrate

(a)

capping layer

electrode with
pinning
INTERLAYERS

adhesion layer

interfacial barrier

substrate

(b)

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

(a)

(b)

Figure 10