Investigation of High-Temperature Degradation of Platinum Thin Films with an In Situ Resistance Measurement Apparatus

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Abstract— Many microfabricated systems require metallizations that can withstand high temperatures. In particular, a microfabricated chemical reactor system which we are investigating needs thin metal films for heating and temperature sensing that can withstand prolonged 1000 °C exposure. The current microreactor metallization, a 100-nm platinum film with a 10-nm titanium adhesion layer, degrades at temperatures greater than 700 °C. This degradation was examined with a custom-built high-temperature resistance measurement apparatus in addition to chemical analysis, scanning electron microscopy (SEM), atomic force microscopy (AFM) and wafer curvature measurements. Thicker films and coating layers increased the lifetime of these films while exposure to oxygen decreased lifetime, consistent with the hypothesized degradation mechanism of agglomeration.

I. INTRODUCTION

HIGH-TEMPERATURE metallizations are desirable for many microelectromechanical devices that must operate under harsh conditions. In microfabricated chemical reactor systems (microreactors), for example, metallizations that can endure prolonged exposure to temperatures greater than 1000 °C are desirable for applications such as heating and temperature sensing, as many reactions of commercial interest require this temperature regime [1]. In MIT’s microreactor design [2], platinum was initially chosen for the heater and sensor metallizations because of its high melting point (1769 °C), resistance to oxidation, nearly constant bulk resistance temperature coefficient and ease of deposition. However, during operation, the 100-nm platinum films (adhered to silicon-rich silicon nitride by a 10-nm titanium adhesion layer) were observed to degrade by forming holes and eventually segregating into unconnected islands, while the resistance of the metallizations was unstable and therefore unsuitable for sensing and heating applications. This degradation phenomena for platinum thin films has also been observed by other groups [3]–[6]. The focus of this work was therefore to characterize and explain this degradation and thereby to find ways of extending the operating temperature range of platinum thin-film heaters and temperature sensors.

We believe that the dominant degradation mechanism is agglomeration, the decomposition of a thin continuous film into a collection of beads. Agglomeration is driven by the high surface to volume ratio of thin films. Surface diffusivity, which is rapid for platinum in the temperature regime of interest (∼1.0 × 10^-6 cm^2/s at 900 °C [7]), acts to reduce the surface area through capillarity [8]. Agglomeration is a nucleation and growth process. Other phenomena such as voids or pinholes must first establish a hole greater than the thermodynamic critical radius, which is determined by film thickness and wetting angle [9]. Once the critical radius is achieved, the hole will grow through capillarity until the film reaches the minimum energy configuration. Degradation via agglomeration has been documented for thin films of gold [10], silver [11], and platinum silicide [12].

Our model for degradation has two stages. In the first stage, the platinum grain boundaries form grooves in the manner first presented by Mullins [13]. The grooves cut through the platinum film and form holes, a process which is aggravated by stress in the film. In the second stage, the holes grow by surface diffusion until the thin film is transformed into unconnected, hemispherical islands. The effect of oxygen enhancing degradation, observed by other groups [3], [5], was also observed in this work. It is argued here that oxygen enhances the agglomeration by diffusing through the platinum grain boundaries and oxidizing the titanium, diminishing the adhesion of the platinum film and consequently aggravating agglomeration.

In this work, the platinum degradation was studied by conventional means as well as by monitoring resistance changes at high temperature with a custom measurement apparatus. A resistance-monitoring technique was used because resistance stability was more important than the film morphology for the microreactor application, which uses resistive heating and resistance temperature device (RTD) temperature sensing. Measuring the resistance of the films while they were heated allowed us to quantitatively monitor degradation. Our measurement system also allowed us to investigate more robust materials combinations that extended the temperature range of the platinum thin films.

II. EXPERIMENTAL DESIGN

This work was done in conjunction with a microfabricated chemical reactor system project in which Srinivasan et al. [2] have built a microreactor for gas-phase catalytic partial-oxidation reactions. The reactor channel has a silicon-
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Fig. 1. (a) A schematic of the test set up for taking a four-point resistance measurement at high temperature. The ambient is controlled by flowing gas through the tube and exhausting the gas at the tube entrance. (b) A close-up of the sample jig. (c) A sketch of the metal pattern on the sample.

rich silicon-nitride membrane structure with 100-nm platinum lines, adhered to the membrane with a 10-nm titanium layer, used as resistors for heating and temperature sensing. The resistors on the test samples for this materials study were designed to mimic the resistors in the microreactor. The samples also underwent a fabrication sequence as similar as possible to the microreactor process.

The test samples were metal lines on nitride-coated silicon die. The metal pattern had eight resistors and one large central pad to facilitate chemical analysis [Fig. 1(c)]. Each of the resistors had four bond pads to allow a four-point resistance measurement, which reduced the effect of contact resistance. The resistors have the dimensions of resistors used in the microreactor. The metals were evaporated onto the sample with an electron-beam system without breaking vacuum between the adhesion layer and the platinum layer. Lift-off patterning was used. After patterning, the samples were sintered at 650 °C for 1 h in nitrogen.

The sample was mounted onto an alumina jig and placed in a tube furnace (Fig. 1). The jig not only supported the sample, but also allowed electrical connections to be made to the sample from the outside. The furnace ambient was controlled with a vent box attached to the tube entrance and a flow of nitrogen or compressed air through the tube from the back at 150 mL/min. The vent at the entrance combined with the incident flow caused external air entering through the box with the connecting wires to enter the vent instead of the tube.

The four-point resistance measurement was conducted with sensing currents of about 1 mA, which corresponded to a current density of 200 A/cm² in the 50-µm-wide lines, and the typical voltage drop was about 110 mV at room temperature. A thermocouple, which was also mounted on the sample jig,
was used to measure the temperature as well as to control the furnace.

The base plate of the jig was cast out of alumina using a wax mold. Wires made of an iron-chromium-aluminum alloy, designed to withstand high temperatures for long periods of time, were run through foot-long 1/8-in-diameter alumina tubes attached to the base plate with high-temperature cement. The ends of the wire were spot welded to small pieces of platinum foil. Wedge bonding with preannealed 25-μm-diameter platinum wire connected the foil to the contact pad. The K-type (chromel/alumel) thermocouple was also brought in through alumina tubes and attached so that the junction was close to the sample.

Because of the work function difference, there was a temperature-dependent voltage drop at the junction between the Fe-Cr-Al alloy wire and platinum foil. However, all of the voltage measurements were symmetric with junctions on both ends of the sample resistor, so that the voltage differences should cancel out as long as the junctions were at the same temperature. This was tested by spot welding two pieces of alloy wire to a strip of Pt foil and placing it in the furnace. The total voltage drop was measured to be negligible and not dependent on temperature.

Two types of tests were run on this system: temperature scans and hold tests. Temperature scans, where the resistance was monitored as the temperature was ramped at a known rate, provided a qualitative measure of the onset of degradation. In hold tests, the sample was brought up to a set temperature at 10°/min and then held as the resistance was measured every minute. The time required for a five percent deviation in the resistance was recorded as indicative of the lifetime of the metallization at that temperature. Hold temperatures ranged from 800 to 1000 °C; the narrow range was chosen because at lower temperatures, change took place too slowly to be time efficient, and at higher temperatures, the resistance had already begun to deviate by the time the hold temperature was reached. The standard deviation in the time measurements ranged from 3% to 13%. A ±2 °C error in the temperature controller and a ~2% variation in film thickness were responsible for the bulk of error.

III. Results

A scan of the resistance, taken at the rate of 5°/min is shown in Fig. 2. While the resistance was well behaved up to ~900 °C, at higher temperatures the resistance quickly increased and displayed drift. When slower heating rates were used, the deviation occurred at lower temperatures. Before proceeding further with quantitative analysis of the degradation, microscopy, chemical analysis, and surface profilometry were used to obtain a qualitative understanding of the mechanism.

A. Microscopy, Chemical Analysis, and Surface Profilometry of Ti–Pt Films

Scanning electron microscopy (SEM) was used to observe the microscale morphology variation over time (Fig. 3). Holes formed in the film after just being brought up to 900 °C, the holes increased in size as exposure time increased until the film had the topography of microscale ridges and valleys. This transformation was observed to occur more rapidly at higher temperatures.

Auger electron spectroscopy (AES) was used to analyze the composition of the films after heating to 1100 °C (Fig. 4). Sputter rate was calibrated to depth by sputtering through an untreated sample with known film dimensions. In examining these untreated films, oxygen was discovered at the titanium-platinum interface. This was probably incorporated during the film evaporation. Even at pressures of 10⁻⁷ torr, there is enough oxygen in the evaporation chamber to be incorporated into the titanium [14].

The AES revealed that the bulk of the coalesced structures was platinum, while oxygen and titanium were found in the valleys. Sputtering through the platinum hills, some silicon was found as the sputter crater approached the nitride underneath the films, revealing the formation of a platinum silicide. Surprisingly, no titanium was found between the platinum and nitride. This could, however, be the result of charging obscuring the measurement as the conducting layer was lost.

Electron-beam sputtered neutral mass spectroscopy (SNMS) confirmed the presence of TiO in the samples. There was also some indication of possible Ti–Pt compound formation in the air-treated samples. Cross sections of an atomic-force microscopy (AFM) image of a sample that had been heated to 1100 °C in air and held there for 10 min revealed that the average height of the platinum in the ridges had more than doubled to ~220 nm (Fig. 5). The surface area of the platinum film after heating was estimated from an SEM. The surface area was found to have been reduced to about 45% of its original value. Combined, these numbers indicate that the volume of the platinum remained constant during heating, which is consistent with our AES observation that the bulk of the platinum did not undergo chemical reaction.

B. Quantifying Ti–Pt Degradation with Resistance Measurements

Hold tests were used to quantify degradation in the 10-nm Ti/100-nm Pt films. As expected, the resistance change rate increased with temperature (Fig. 6). The effect of oxygen in the ambient was tested by comparing the behavior in air...
Fig. 3. SEM images show the formation and growth of holes in the Ti–Pt film. (a) After 0 h at 900 °C. (b) After 2 h at 900 °C. (c) After 6 h at 900 °C. (d) After 9 h at 900 °C.

Fig. 4. AES results suggested that some oxygen was already incorporated into the adhesion layer during evaporation. After heating, AES revealed that the bulk of the coalesced structures was platinum, while oxygen and titanium were found in the valleys.

with the behavior of the metallization in nitrogen. A sample was brought up to 900 °C in nitrogen and held for 112 min. After 100 min, the resistance was observed to be increasing at the rate of 3%/h. When the environment was switched to air, the resistance increased sharply at first and then continued to increase at more than 5%/h (Fig. 7). Hold tests were conducted at 900 °C for Ti–Pt samples in both air and in nitrogen. The sample in the nitrogen ambient had a lifetime of 87.5 min, which was twice that of the 44-min lifetime observed for the films heated in air.

While most of the tests were performed on substrate-supported films, Ti–Pt films suspended on nitride membranes were also observed in order to characterize the effect of the membrane. The membrane films had the same postanneal morphological appearance as the substrate-supported films. However, lifetimes were significantly longer for membrane metallizations: 125 min rather than an average lifetime of 44 min at 900 °C.

C. Behavior of Ta–Pt Films

An alternative hypothesis for the degradation mechanism was that the observed phenomenon was the result of eutectic formation with the titanium. Titanium and platinum form a eutectic at 840 °C, and tantalum and silicon form a eutectic at 865 °C. Tantalum, which is another metal that can be used as an adhesion layer for platinum, does not form eutectics with platinum and silicon below 1635 and 1400 °C, respectively. In order to eliminate the eutectic hypothesis, samples were
fabricated with tantalum instead of titanium as the adhesion layer.

SEM images of the tantalum-adhered films showed that the films had fewer holes than the Ti–Pt films just after fabrication and that the morphological changes of the films during heating were similar to the titanium-adhered films. AES results were also similar to those of the Ti–Pt films: oxygen and tantalum were found in the valleys, platinum made up the bulk of the coalesced structures, and there was evidence of silicide formation near the Pt–nitride interface. SNMS yielded similar results as well, confirming the oxidation of the adhesion layer. Unlike the Ti-adhered samples, there was no evidence of compound formation with the platinum. The hold measurements revealed that the tantalum-adhered films had a significantly longer lifetime than the titanium-adhered films. The 5% deviation time at 900 °C increased from 44 to 220 min with the use of tantalum as the adhesion layer material.

D. Thickness Dependence of Degradation

The dependence of the degradation phenomena was explored with Ta–Pt samples because of the improved lifetime of Ta-adhered films. Three thickness variations were tested in addition to the standard 10-nm Ta/100-nm Pt samples: 20-nm Ta/100-nm Pt, 10-nm Ta/200-nm Pt, and 10-nm Ta/400-nm Pt. Doubling the tantalum thickness drastically reduced the lifetime of the films at 900 °C from 220 to 43 min. Doubling the platinum thickness increased the lifetime from 220 to 985 min. The 900 °C lifetime of the 400-nm Pt samples was 2880 min.

E. Behavior with Capping Layers

The lifetime improvement that resulted from annealing in an oxygen-poor environment motivated the fabrication of samples with coatings that would act as oxidation barriers. Silicon nitride and alumina coatings were both used.

The resistance of the samples coated with 1000-Å silicon nitride showed complex behavior during the temperature scan. The films appeared bubbly in the optical microscope, and AES revealed platinum in addition to silicon and nitrogen in the nitride layer. This suggests that a platinum silicide layer formed during the deposition of the plasma-enhanced chemical-vapor deposition (PECVD) nitride and that the resistance change is indicative of that layer growing and experiencing phase change.

The addition of the 3000-Å alumina adhesion layer, however, dramatically improved the behavior of the films. The average lifetime of the Ti–Pt films at 900 °C improved from 44 to 292 min with the addition of an alumina layer. The results for all of the 900 °C hold tests are summarized in Table I.

F. Wafer Curvature Measurements

Wafer curvature measurements (Fig. 8) were made on three wafers: one coated only with 1 μm of nitride, one with 1-μm nitride/10-nm Ti/100-nm Pt, and one with 1-μm nitride/10-nm Ta/100-nm Pt. Each wafer was brought up to 900 °C at 10°/min, and the curvature measured every 2 min. The temperature was held at 900 °C for 20 min before returning to room temperature at about 10°/min.

The curvature of all the samples remained constant during the 20-min hold at 900 °C. The films were found to be tensile as deposited. This is to be expected because the wafers in the evaporator were probably well above room temperature when the platinum was deposited. The films became less tensile with increasing temperature, which we expect from the thermal expansion mismatch between the films and nitride. The films are less tensile after the thermal cycle, indicating that some stress relaxation did take place, only it was relaxation not of the compressive stress induced by heating, but relaxation of the tensile stress incurred in deposition.

IV. DISCUSSION

To summarize the data: degradation was retarded by oxygen-poor ambients, thicker Pt films, alumina coating layers, suspension on a membrane, and the use of Ta as an adhesion layer instead of Ti. Degradation was accelerated by thicker adhesion layers and higher temperatures. SEM showed that the film formed holes which grew over time. AES indicated oxidation of the adhesion layer and silicide formation near the interface for both the Ta- and Ti-adhered films.
The nitrogen/air studies and composition analyzes indicate that oxygen plays a role in the degradation. However, oxygen diffusion and reaction does not appear to be the dominant mechanism in the degradation. The observed morphological changes are not consistent with oxidation being dominant, and the strong dependence of the lifetime on the adhesion layer thickness is not consistent with the rate being limited by oxygen diffusion through the platinum layer.

The data also shows that eutectic formation is not the driving mechanism. In the Ta–Pt samples, where eutectic
The relaxation probably took place at intermediate temperatures, where the atomic mobility was sufficient for relaxation while the tensile stress was still large. This is not consistent with stress relaxation motivating the morphological changes, which we know from the resistance measurements to occur during 900 °C holds. It is, however, possible that the tensile stress contributes to hole formation, which is preliminary to the growth of the holes and subsequent resistance change.

All of these observations are consistent with the agglomeration hypothesis discussed above. The lifetime is a strong function of temperature, which is consistent with the Arrhenius behavior of surface diffusivity, which drives agglomeration. The observations of oxygen diffusion enhancing degradation are consistent, as the oxygen at the Ti–Pt and Ta–Pt interface would reduce the adhesion of the platinum layer.

The increased lifetime of Ta–Pt films compared to Ti–Pt films might be due to titanium’s greater affinity for oxygen, or to the difference in pinhole density observed for the as-deposited films. This difference in pinhole density could in turn be a consequence of differences in oxygen affinity, or a difference in the deposition conditions. Also, Ti–Pt eutectic formation could enhance the agglomeration effect.

The thicker adhesion layer increased the amount of oxygen at the interface, further reducing the adhesion of the platinum film and hastening agglomeration. Membrane-supported films had longer lifetimes than substrate-supported films because the films on the membrane were able to relieve some of the large tensile stress through deflection, and stress enhances agglomeration by hastening hole formation. Doubling the platinum thickness resulted in a 4.5-fold increase in lifetime, and quadrupling the platinum thickness resulted in a 13-fold lifetime increase. The trend is consistent with Jiran’s and Thompson’s observation that the hole growth rate is a strong function of thickness, but they predicted an inverse cubic dependence [10]. This data, however, reflects both hole formation and hole growth and, therefore, is not directly comparable.

These results suggest several possible solutions for increasing the lifetime of thin-film metallizations at high temperatures. The most simple solution is to use thicker films. In addition to increasing the hole growth rate, thicker films also increase the size required for the initial hole to be thermodynamically favored to grow, as well as the depth of groove required to form the hole. Srolovitz and Safran [15] predict that the thermodynamic equilibrium groove depth $d$ of a film, with a grain size $2R$ and an equilibrium notch angle $\Phi$, is given by

$$d = R \frac{2 - 3 \cos \Phi + \cos^2 \Phi}{3 \sin^2 \Phi}. \quad (1)$$

Assuming a grain size of 2 $\mu$m, which is about the largest size observed in the SEM images, and the worst case notch angle of $90^\circ$, the equilibrium groove depth could be as large as 667 nm. Although it should be noted that (1) was derived for the intersection of two grains; where three grains intersect groove depths are larger. Metal layers as thin as 1 $\mu$m might be sufficiently thick to avoid agglomeration. In addition to demonstrating the increased longevity of thicker films, this work has also shown that coating layers increase the lifetime of platinum films, as well as the use of tantalum adhesion layers.

Also, other refractory metals might be considered instead of platinum. As a rule of thumb, the surface diffusivity at a given temperature will be smaller for a material with a higher melting point. Iridium, for example, melts at 2407 °C, Silicides might also be considered. Platinum silicide is not a potential candidate, because it has been observed to be unstable at temperatures above 600 °C [12]. Many silicides, including PtSi, CoSi$_2$, WSi$_2$, and MoSi$_2$ are unstable in high-temperature oxidizing ambients. TiSi$_2$, however, is known to be stable in high-temperature oxidizing ambients both when supported on SiO$_2$ and when supported on Si [16]. The use of silicides would complicate the metallization process, but might be a solution if the other measures are insufficient.

V. CONCLUSIONS

In conclusion, this work combined chemical analysis, microscopy, and a custom-built in situ resistance measurement technique to examine the high-temperature behavior of the titanium-adhered platinum films used for heating and temperature sensing in a silicon-based microfabricated chemical reactor system. Many mechanisms appear to play a role in the degradation of thin platinum films, including stress and interlayer reaction, but the dominant mechanism is agglomeration, a surface-diffusion-driven capillarity process. Tests with alumina-coated and double- and quadruple-thickness samples demonstrated that the lifetime of the metallizations can be increased by making the platinum thicker, adding coating layers and using tantalum as the adhesion layer, all of which is consistent with the hypothesized agglomeration degradation mechanism.

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