Effects of Thermal Annealing on the Electrical Properties and Stability of Pt Thin Film Resistors with Ti and Pt$_x$O$_y$ Interlayers

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Abstract. Influences of annealing temperature on microstructure, electrical properties, stability, and film adhesion of Pt thin film resistors with Ti interlayer and Pt$_x$O$_y$ interlayer were investigated and compared. Pt thin films were deposited on Al$_2$O$_3$ substrates with Ti interlayer and Pt$_x$O$_y$ interlayer, respectively. Two resistors showed different microstructures after annealing. Pt/ Pt$_x$O$_y$ film resistor owed more stable resistance value and larger temperature coefficient of resistance (TCR) than those of Pt/Ti film resistor. Annealed Pt/Ti film resistor exhibited poor stability than Pt/ Pt$_x$O$_y$ film resistor and the stability became worse with increasing annealing temperature. In addition, the film adhesion of two resistors was discussed.

Keywords: Pt thin film resistor, Annealing, Interlayer, TCR, Stability

1. Introduction

Platinum thin film resistor is popular in industry for the advantages of small size, high stability, and fast response. Pure Pt film does not adhere well with substrate like Al$_2$O$_3$ or SiO$_x$ because of mismatching, therefore interlayer between Pt film and substrate is often used to improve film adhesion. The interlayer should be prone to form stable bond with substrate, and metal like titanium (Ti), tantalum (Ta), or chromium (Cr) is commonly used. However, interdiffusion, interlayer oxidation and reaction with Pt or substrate always lead to the increase of resistance and decrease of TCR and stability [1-6]. X. Lin observed that with increasing annealing temperature, resistance increase rate kept reducing and TCR increased when annealed at above 500 °C because of recrystallization process. The maximum TCR was 2980 ppm/°C lower than that of bulk Pt resistor of 3850 ppm/°C [1] when annealed at 800 °C. Higher annealing temperature worth exploring.

The easily oxidized metal has better adhesion to the oxide substrate [7]. It is not except for the natural oxidation of Pt, but Pt$_x$O$_y$ film can be prepared by reactive magnetron sputtering in O$_2$/Ar gas mixtures [8]. Study showed Pt/Pt$_x$O$_y$ film owed a strong film adhesion even after several thermal cycling at 1000 °C [9]. In this paper, Pt thin film resistor with Pt$_x$O$_y$ interlayer and the influences of sputtering parameters, like power, pressure, and oxygen partial pressure O$_2$/(O$_2$+Ar), and annealing condition on film loss, stress, resistivity, and film adhesion were investigated and optimal preparation parameters were given. But the TCR and stability were not considered.

In this paper, Pt thin film resistors with Ti interlayer and Pt$_x$O$_y$ interlayer were prepared, respectively,
and then annealed in the range of 800 °C ~ 1000 °C for 2 h. For both resistors, the influences of annealing temperature on film microstructure and resistance change rate were investigated. The TCR and stability of two resistors were compared. In addition, the film adhesion was tested.

2. Experimental

2.1. Pt Thin Film Resistor Preparation
Thin film resistors were fabricated by depositing interlayer film and Pt film on Al₂O₃ substrate, and annealing at different temperature for 2 h. For resistor with PtₓOᵧ interlayer, the PtₓOᵧ film was deposited by reactive magnetron sputtering. The mixture of oxygen and argon was used as sputtering media. The Pt film was deposited by RF magnetron sputtering in pure argon without breaking the vacuum. Thin film resistors were patterned by lithography and lift-off process. The preparation process was the same for resistor with Ti interlayer except the interlayer was deposited by magnetron sputtering with 99.99% pure titanium target in pure argon.

The substrates were cut into individual samples with the size of 7.7 mm x 7.7 mm x 0.6 mm then annealed in air at different temperature for 2 h. Figure 1 showed the optical image of Pt thin film resistor.

![Figure 1. An image of Pt thin film resistor.](image)

2.2. Resistor Characterization
Digital Microscope (Keyence, VHX-5000, Japan), and Scanning Electron Microscope (SEM, Zeiss ultra 55, Germany) were used to examine the surface microstructure. TOF-SIMS (TOF-SIMS, ION TOF TOF-SIMS 5-100, Germany) was used to detect three-dimensional spatial scale chemical composition distribution by depth profiling.

The film adhesion was measured by nanometer scratch meter (CETR UMT-3, Bruker, USA) with a spherical diamond tip (2 μm radius of curvature). During the test, a vertical load was applied on the tip and increased from 0 mN to 450 mN at a constant speed in 3 min, meanwhile, the tip moved horizontally by 3 mm. The critical load (Lc) when a large area of film peeling off was used to characterized film adhesion.

2.3. TCR and Stability
The temperature dependence of the resistance was measured in an intelligent thermostatic oil bath between 20 °C~150 °C by heat equipment and the resistance was measured by A 6½ digital Agilent multimeter (Agilent, Keysight 34464A, USA). At low temperature, the resistance changes linearly with temperature and the average TCR was calculated by the following formula:

\[
TCR = \alpha = \frac{R_{T_2} - R_{T_1}}{R_0(T_2 - T_1)} = \frac{\Delta R}{\Delta T \cdot R_0}
\]

Where \(R_0\) is resistance value at 20 °C.

Stability was characterized by repeatability of R-T curves with the test temperature range from room
temperature to annealing temperature.

3. Results and Discussion

3.1. Effect of Annealing on Microstructure

Pt thin film resistors with Ti interlayer and Pt$_x$O$_y$ interlayer were heated at muffle furnace up to 800 °C, 900 °C and 1000 °C for 2 h, respectively, and cooled naturally. It was noticed that Pt/Ti film lost its metallic luster after annealing. The images of surface topography were showed in figure 2. It was observed that Pt resistors with two different interlayers exhibited different surface topography.

![Figure 2](image_url)

After annealing at 800 °C, grains with diameter in the range of 0.1 μm to 1 μm were observed and irregularly distributed on the Pt/Ti film surface. This was associated by recrystallization process and followed by nucleation and grain growth to form relatively defect-free grains and more stable microstructure [1, 9]. Besides, film agglomeration and voids occurred (figure 2(a)). While there were some bubbles (2 μm to 20 μm in diameter) on the surface of annealed Pt/Pt$_x$O$_y$ films as shown in figure 2(d). Figure 3 showed the depth profiling plots and 3D render images of as-deposited and 800 °C annealed Pt/ Pt$_x$O$_y$ film. Ion gun was applied to sample surface during the depth profiling experiment, and the test area was 100 μm × 100 μm. Figure 3(a) and (c) showed the intensity change of ions (Pt-, PtO-, PtO$_2$-, AlO-) with sputter time. Pt- ion represented the present of Pt containing materials like Pt, PtO, and PtO$_2$. PtO- indicated the present of PtO or PtO$_2$. PtO$_2$- and AlO- meant PtO$_2$ and Al$_2$O$_3$, respectively. The longer time the sputtering took, the deeper the sputtering depth was. Figure 3 (b) and (d) were 3D render images. It was clear about the composition distribution of Pt/ Pt$_x$O$_y$ film resistor, including the upper Pt film, the Pt$_x$O$_y$ (PtO and PtO$_2$) interlayer and Al$_2$O$_3$ substrate. Moreover, the concentration of Pt$_x$O$_y$ reduced and Pt diffusion got serious after annealing. Pt$_x$O$_y$ interlayer film was deposited by reactive magnetron sputtering in O$_2$/Ar gas mixtures which agreed with previous studied [8,10] and Pt$_x$O$_y$ will break down at 550 °C to form Pt, PtO and O$_2$ and completely dissociate into Pt and O$_2$ under 1100 °C [2,3,11]. The existence of bubbles may be explained by decomposition of Pt$_x$O$_y$ and escape of oxygen. As the annealing temperature increasing, for Pt/Ti film, the size of grain increased and film agglomeration got worse. At the same time, the bubbles slightly reduced in size for Pt/ Pt$_x$O$_y$ films (figure 2(e)) which can be explained by the decomposition of Pt$_x$O$_y$ was weakened. When annealed at 1000 °C, the Pt/Ti film came into being isolated islands and grain became much denser. For 1000 °C annealed Pt/ Pt$_x$O$_y$ films, the number and size of bubbles were significantly reduced (figure 2(f)) and the bubbles became sunken. And the film agglomeration and voids were obviously observed on the edge of film (not shown in the text). All the images illustrated thermal annealing had greater effects on the microstructures of Pt/Ti film and Pt/ Pt$_x$O$_y$ film.
3.2. Effect of Annealing Temperature on TCR and Stability

After annealing, the temperature dependent resistance behavior was tested. Table 1 showed annealing temperature on the average resistance changes rate of resistors with Ti interlayer and that with Pt$_x$O$_y$ interlayer. A positive resistance change rate indicated an increase in resistance after annealing, and vice versa. It was observed that Pt/Ti film resistance increased after annealed at 800 ℃ and 900 ℃ which could because of interdiffusion of Pt and Ti [1], the formation of Ti–Pt compound [2] and film agglomeration. In fact, the resistance began to increased when annealed at 500 ℃ and the change rate of resistance even reached 227%, and then it gradually decreased as the annealing temperature increased [1]. With increasing annealing temperature, the average resistance changes rate kept decreasing and became negative at 1000 ℃, this indicated the effects of grain growth and recrystallization on resistance were gradually significant. The resistance of Pt/Pt$_x$O$_y$ film resistor decreased after annealing and annealing temperature had few effects on resistance change rate. It indicated the influence factors, like grain growth, Pt$_x$O$_y$ decomposition and film agglomeration, achieved balance.

Table 1. Effect of annealing temperature on resistance change rate of resistors with different interlayers.

| Interlayer | Annealing temperature (℃) |
|------------|---------------------------|
|            | 800          | 900          | 1000         |
| Ti         | 20.0%        | 9.8%         | -3.0%        |
| Pt$_x$O$_y$| -32.4%       | -32.9%       | -32.6%       |

Figure 4 showed the TCR dependent on annealing temperature of two resistors. TCR was determined by initial resistance and the slope of resistance temperature curve (R-T curve). It was observed that the TCR and the slop of R-T curves of both resistors increased with increasing annealing temperature (not shown in the text) and the TCRs of Pt/Pt$_x$O$_y$ film resistors were larger than those of Pt/Ti film resistors during the whole annealing temperature. Pt/Ti film resistor owed low TCR when annealed at 800 ℃ and
900 °C, which was mainly caused by the increase in resistance after annealing. The TCR of Pt/Pt$_x$O$_y$ film resistor and Pt/Ti film resistor reached 3434 ppm/°C and 3421 ppm/°C when annealed at 1000 °C, respectively.

Stability was very important for practical application and the R-T curves of both resistors were tested for 3 or 4 cycles under the testing temperature from 250 °C to their annealing temperature, as illustrated in figure 5. Compared with Pt/Ti film resistors, Pt/Pt$_x$O$_y$ film resistors exhibited better repeatability of R-T curves. The poor repeatability of Pt/Ti film resistors showed that although resistors annealed at 900 °C or above owed higher TCR, they cannot work steadily. The repeatability of 900 °C annealed resistors was better than that of 1000 °C annealed resistors, especially at low temperatures. 900 °C annealed Pt/Pt$_x$O$_y$ film resistor was optimal for practical application under 900 °C because of high TCR and stability.

Figure 4. TCR vs. annealing temperature curves of Pt/Ti film resistor and Pt/Pt$_x$O$_y$ film resistors.

Figure 5. R-T curves of Pt/Ti film resistors (a, b) and Pt/Pt$_x$O$_y$ film resistors (c, d) annealed at 900 °C (a, c) and 1000 °C (b, d).

Figure 6 showed the SEM micrographs of Pt/Ti film resistors and Pt/Pt$_x$O$_y$ film resistors after cycle
testing. The voids were observed for all samples and they were more dense and smaller in size for Pt/Ti film resistors than those of Pt/PtOy film. The voids of 1000 °C annealed films were more serious than those of 900 °C annealed films which suggested the annealing temperature of Pt/PtOy film resistors showed be under 1000 °C. For Pt/Ti film resistors, annealing temperature was advised be below 900 °C. The severity of film voids agreed with the repeatability of R-T curves. Figure 6(c), (f) were further blowup of figure 6(b), (e), and obvious grain growth and grain boundaries can be observed.

![SEM micrographs of Pt/Ti film resistors (a, b, c) and Pt/PtOy film resistors (d, e, f) annealed at 900 °C (a, d) and 1000 °C (b, c, e, f) after cycle testing.](image)

3.3. Effect of Annealing Temperature on Film Adhesion

Film adhesion of Pt/Ti film and Pt/PtOy film was tested, as illustrated in table 2. “>450 mN” meat overload. Pt/Ti films were with good film adhesion that Lcs were always overload in the entire annealing temperature range because of interdiffusion and Pt-Ti bonding [3], and were larger than the film adhesion of Pt/PtOy films. Film adhesion of Pt/PtOy films reduced as annealing temperature increased, which can be explained by the decrease of oxygen content and oxygen-to-oxygen bond strength due to PtOy decomposition [11]. In conclusion, Ti interlayer ensure good film adhesion for Pt thin film resistor even annealed at 1000 °C and Pt/PtOy film resistor showed acceptable film adhesion, especially annealing at slightly lower annealing temperature.

| Interlayer | Annealing temperature (°C) |
|------------|----------------------------|
| Ti         | >450  >450  >450           |
| PtOy       | >450  329   206            |

4. Conclusion

Pt thin films with Ti interlayer and PtOy interlayer were deposited on Al2O3 substrates, respectively. The effects of annealing temperature on microstructures, TCR, high temperature stability and film adhesion of Pt/Ti thin film resistors and Pt/PtOy interlayer were investigated. Pt/Ti film recrystallized and film agglomeration occurred when annealed at 800 °C. For annealed Pt/PtOy film, PtOy break down to form O2 which escape to form bubbles on the film surface. With increasing annealing temperature, the TCR of Pt/Ti film resistors increased significantly, but film became isolated islands and resistors showed poor stability. The film adhesion of Pt/PtOy film was not strong as Ti/Pt film, but owed larger TCR and higher stability. Pt/PtOy film resistor annealed at 900 °C was optimal for practical application.
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