Reliability of platinum electrodes and heating elements on SiO₂ insulation layers and membranes

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Abstract

In this work, failure mechanisms of Pt electrodes including adhesion problems, material migration due to thermally induced compressive stress and electromigration that could occur in the platinum electrodes and heater structures at temperatures above 600 °C have been systematically studied, after the deposition. Lifetime determination, scanning electron microscopy and XRD analysis have been applied for samples which have experienced different loading conditions in order to qualitatively and quantitatively understand the phenomena. Electromigration testing is performed with the aim to enable time-to-failure prediction for sensor elements and compare different platinum layers in terms of their stability. Dedicated, application-related test structures are used so that the results are applicable to sensor lifetime estimations. Furthermore, a method for the determination of thermal conductivity of thin insulating films has been adapted for the characterization of plasma-enhanced chemical vapor deposition (PECVD) silicon oxide and successfully applied on two materials with different deposition recipes. These two materials are used for the fabrication of platinum-based heating elements with PECVD SiO₂ as insulation or membrane layer. The results for the two recipes are similar but with a significant difference. A slight increase of the conductivity has been observed due to a thermal anneal of the test structures at temperatures above 700 °C.

1. Introduction

Human-caused environmental polluting is one of the main challenges of our modern society. One key aspect of environmental protection concerning personal mobility is fuel consumption reduction in combustion engine vehicles by sensor aided engine control [1]. Moreover, the soot particle emission is suspected to cause many respiratory system diseases, so that its reduction by using a diesel particulate filter and monitoring is at least of great importance as well. Gradual improvement of both factors is embedded in the new EU/US emission standards [1], and, thus, the development of appropriate sensors is necessary to reach the according goals.

A simple schematic of a soot particle sensor is shown in Fig. 1 together with the sensor’s position in the exhaust gas system. The functional principle of the soot particle sensor is based on the deposition of soot on its surface, which leads to the formation of electrically conductive paths between the interdigitated thin-film platinum electrodes. When a voltage is applied between the electrodes, an electrical current can be measured that is correlated to the total amount of deposited soot. The sensor can thus be used for monitoring the condition of the particle filter of a combustion engine vehicle. The sensor needs to be regenerated periodically by heating up to a temperature of at least 700 °C to burn the soot deposited on its surface. Such sensors are typically fabricated on a ceramic substrate with sintered platinum electrodes and backside heater elements [2]. Using micromachining methods for the fabrication of such sensors allows for the reduction of the electrode spacing and thus an increase of the sensitivity.

The materials of the soot particle sensor are exposed to the harsh environment of the exhaust gas system of a combustion engine vehicle including temperatures of up to 500 °C and a corrosive atmosphere. During the regeneration phase the temperature can reach values even as high as 800 °C. Therefore, robust materials are required for the soot particle sensor and thin-film platinum has been chosen as electrode and heater material, and silicon oxide as insulation and/or membrane material. The silicon chip of the sensor is mechanically stable for temperatures of at least 900 °C and thin silicon oxide film forms on its surface, which protects it from further degradation in the corrosive atmosphere.

2. Thermal properties of PECVD SiO₂

In the micromachined version of the soot particle sensor, silicon oxide is used as an electrical insulation layer between the platinum electrodes and the silicon-chip substrate. Additionally, a membrane can be formed under the interdigitated electrodes of the sensor by etching the silicon of the chip from the back by KOH or dry reactive etching (DRIE). In this case, a slightly tensile stress condition is required for the stability of the oxide membrane, which should have a thickness of...
of the SiO₂ deposited by PECVD is an important parameter for the sensor to be reliable and to ensure its stability. Therefore, the thermal conductivity should exhibit a significantly higher temperature in order to reduce the load and to ensure its stability. Therefore, the thermal conductivity of the SiO₂ deposited by PECVD is an important parameter for the sensor design. The understanding of its anneal and aging behavior is necessary in order to ensure the sensor reliability and its stability over lifetime.

The method for the determination of thermal conductivity, adopted and successfully applied in this work, is similar to the one presented in [3]. It is based on a micro-machined test structure consisting of a 5 mm long, narrow stripe with a PECVD SiO₂ layer packed between two platinum layers. A schematic cross-section of the test structure is shown in Fig. 2. The upper platinum stripe is operated with high electrical current in order to generate a considerable amount of Joule heat, which flows to the substrate through the structure leading to a significant rise of the temperature difference between the two platinum stripes. The mean temperatures of each of the stripes can be determined from their electrical resistance. The amount of heat flowing through the structure corresponds to the electrical power dissipated in the upper stripe. The lower platinum stripe is operated with very low current to avoid any internal heat-up. The temperature difference \( \Delta T \) and the heat flow \( \frac{dQ}{dt} \) are connected by the equation

\[
\Delta T = \frac{dQ}{dt} \cdot R_\text{th} \text{,}
\]

where the thermal resistivity is defined as \( R_\text{th} = 1 / \kappa \cdot G \) with a thermal conductivity \( \kappa \) of the PECVD SiO₂. \( G \) is a geometry factor. Fig. 3 shows the simulated temperature distribution over the cross-section of the test structure with a temperature gradient from the upper to the lower platinum stripes leading to the heat flow. The terrace-like geometry, necessary to face mask misalignment generated by the exposure tool, leads to colder edges of the lower platinum stripe, which do not contribute to the heat flow. These colder edges reduce the mean temperature of the stripe and this way increase the measured temperature difference to the upper stripe. This effect needs to be corrected for in order to obtain the temperature difference relevant for the heat flow. The correction factors depend on the geometrical parameters of the structure and the actual thermal conductivity of the PECVD oxide layer. They have been calculated to be quite significant between 0.45 and 0.90 using ANSYS FEM simulations and are applied recursively on the measurement results. The FEM simulation shows that heat dissipation to the environment is negligible for temperatures up to 500 °C.

Four different layer thicknesses of the PECVD silicon oxide between 400 nm and 1700 nm have been studied for each of the two PECVD recipes, so that a total of eight wafers have been processed. Each wafer contained twelve test structures separated in two groups: wide test structures with a width of 52 μm for the PECVD SiO₂ stripe and narrow test structures with a width of 22 μm. The measurements are performed at wafer-level using the PA200 Suss probe station with a heat chuck. The temperature of the chuck can be controlled between 10 °C and 300 °C with a precision of 2 °C allowing for the calibration of the resistance-temperature characteristic of the platinum stripes. This characteristic is used for temperature determination of the stripes during the actual experiment when high electrical power is applied to the upper stripe and Joule heating occurs. The Joule heating increases the temperature of the PECVD oxide reaching values almost 150 K higher than those for the chuck temperature. The electrical measurements are performed by a Keithley 2602 source-meter featuring two four-wire channels allowing the simultaneous measurement of the resistance of the upper and lower platinum stripes with variable testing currents. The test structures have been annealed at 500 °C before the measurement of the thermal conductivity in order to stabilize the thermo-electrical properties of the platinum stripes.
The thermal conductivities of the four different layer thicknesses and two structure widths are presented in Fig. 4 as a function of the temperature for up to 450 °C for the stoichiometric PECVD SiO2 recipe. The results for the Si-rich oxide layers show a similar behavior with a slightly lower thermal conductivity. All eight measurements agree well with each other within their uncertainties. This shows that the thermal conductivity of the PECVD silicon oxide layers shows no or only very little thickness dependence. The mean values of the specific thermal conductivity for the two recipes are presented in Fig. 5 together with the values for fused bulk quartz [4] and other measurements for PECVD SiO2 thin films [3]. They are lower than the values for bulk quartz and exhibit a significant difference between each other, which shows the influence of recipe variation on the material properties.

In order to investigate the effect of a thermal anneal at high temperatures on the thermal conductivity of the PECVD SiO2 layers, the test structures have been tempered at 750 °C for 20 h and the measurements repeated. Such an anneal is expected to cause a reduction of the hydrogen content of the layer through diffusion [5] and possibly additional oxidation, especially for the recipe with increased silicon content, which would change the thin-film material properties.

Fig. 6 shows the results of the thermal conductivity measurements for the stoichiometric PECVD SiO2 after the thermal anneal. While the values for the narrow test structures agree with each other and are slightly higher than the results for the non-annealed samples, the values for the wide test structures are significantly lower and deviate strongly from each other. The results for the test samples with Si-rich PECVD oxide show a similar behavior. The only difference to the results for the stoichiometric PECVD SiO2 is that for the Si-rich layers also the narrow structures with the thinnest oxide layer are significantly lower than the results for other narrow structures.

For the investigation of this behavior of the annealed test structures, focused ion beam (FIB) and scanning electron microscopy (SEM) imaging has been applied after the thermal conductivity experiments. An example for the images of the wide test structures is presented in Fig. 7, where the cross-section of the multi-layer stripe is visible. Next to the large, abnormally grown crystallites, which have been studied in detail in our earlier publications [6,7], even larger, “bubble-like” structures are visible on the surface of the upper platinum thin film. They are presumably due to delamination caused by the difference in the coefficients of thermal expansion between the platinum and the silicon substrate leading to high compressive stress in the Pt layer [8]. These structures are visible on all test structures which exhibit lower measured thermal conductivity values. The thermal flow through the interface of the two layers is reduced due to these defects, which artificially reduces the measured thermal conductivity of the PECVD silicon oxide.

For the calculation of the proper values of the thermal conductivity of the SiO2 layers after the thermal anneal, only the results for the narrow test structures have been used, excluding the test samples where delamination has been observed. The resulting thermal conductivities are plotted vs. temperature in Fig. 5. The values for the two recipes have increased compared to the non-annealed samples and are closer to each other, probably due to the increased density of the PECVD silicon oxide [5].

3. Reliability of platinum thin films

As observed for the thermal conductivity test structures, extreme conditions similar to these in the exhaust gas system of a combustion engine vehicle can cause failure even to such a mechanically stable and chemically inert material as platinum. Temperatures above 700 °C...
and high stress conditions due to the mismatch in the coefficients of thermal expansion of the platinum layer and the substrate can lead not only to adhesion issues but also to grain growth and material relocation due to stress migration. Moreover, at these high temperatures the diffusivity of foreign atoms within the platinum increases so that they can diffuse into the layer and alter its properties. In addition, electromigration phenomena can occur in the platinum structures of the soot particle sensor due to the high current densities in the electrodes which are necessary to produce the high temperatures.

For the investigation of these phenomena and especially of the electromigration-caused failure in the platinum structures, qualitative and quantitative experiments have been designed and performed on various platinum thin films. These platinum films and their Ti or Ta adhesion layers are deposited by DC magnetron sputtering to typical thicknesses between 300 and 500 nm. Some results have been already presented in [6,7]. Here, additional results will be presented and the electromigration lifetime of the layers will be related to the material evolution at high temperature. The parameters of Black’s equation [9] will be shown for Ti and Ta adhesion layers, Ti alloying of the Pt layer, and for SiO2 passivation.

Fig. 8 presents the XRD spectra of platinum thin films without an adhesion layer around the platinum {111} peak before and after thermal annealing at 730 °C for 20 h in air and N2 atmospheres. The shift of the main peak corresponds to a change of the distance of the crystallographic planes parallel to the surface towards smaller values, probably due to a more tensile stress condition of the layer. The narrowing and splitting of the main peak into several peaks suggests the development of a multimodal grain size distribution, with different plane distances.

The distribution may consist of platinum grains with higher mean grain sizes compared to the non-annealed samples. The grain growth has also been observed in FIB/SEM images of “as deposited” and annealed platinum layers presented in [7]. In addition to these results, a platinum (100) peak emerges after the thermal annealing as shown in Fig. 9. This (100) peak could correspond to the abnormally grown grains since the grain orientation is expected to affect the growth rate [10]. The XRD results of the platinum samples with Ti adhesion layer are very similar to the results for the pure-platinum samples shown here with the difference that the (100) peaks are less pronounced.

In order to investigate the effect of the phenomena taking place in the platinum layer, the resistivities of five platinum samples have been measured before and after a thermal anneal at 730 °C for several hours. Fig. 10 shows the resistivity values for the non-annealed samples and Fig. 11 shows the results for the platinum samples annealed in air. The non-annealed pure-platinum sample shows a linear resistivity-temperature characteristic, with reduced resistivities after the thermal anneal due to the grain growth. The platinum with a titanium adhesion layer shows a resistivity that grows stronger than linear above 300 °C, probably due to diffusion of titanium atoms into the platinum and alloy formation, which reduces the electrical conductivity [11]. After the thermal anneal the resistivity-temperature characteristic becomes linear and the resistivity reduces. The titanium reacts with the oxygen diffusing into the platinum [7] and is, this way, removed from the solution, and its effect on the resistivity is strongly reduced [12]. The platinum samples with 10 vol.-% titanium addition have higher resistivity values,
but show a similar behavior. For the non-annealed samples with tantalum adhesion a linear resistivity–temperature characteristic is observed, but the resistivity reduces after the thermal anneal to values close to the ones of the Ti-adhesion samples, thus a similar diffusion-based material evolution can be assumed.

The passivated platinum samples show a higher resistivity compared to all other platinum layers, since they have been heated up to 400 °C for several minutes during the deposition of the passivation PECVD oxide and the titanium has already diffused into the platinum, reducing the electrical conductivity of the layer. During the heat-up of the non-annealed samples, the resistivity grows stronger than linear, probably due to further diffusion of titanium into the platinum. The annealed samples show a higher resistivity compared to the non-annealed ones due to blocking of oxygen during the annealing by the passivation, and the titanium remaining in solution in the platinum.

Electromigration [9] can cause failure in thin-film heater elements due to an effective depletion of material caused by an unbalanced flow of platinum atoms. This phenomenon can take place on a macroscopic scale due to temperature gradients or current density divergences or on a microscopic scale in the grain boundaries of the platinum. A detailed comparison between the electromigration-driven failure on a macroscopic and microscopic scale has been presented in [7]. Although it is almost impossible to fully avoid temperature gradients and current density divergences, the design of a heater element should aim to minimize them, since they are extremely critical for the device reliability and strongly reduce its lifetime.

Current density divergences and temperature gradients almost always occur in real heater elements. It is, nevertheless, necessary to study optimized test structures, where the damage forms on a microscopic scale due to current density divergences in the grain boundaries. In this case, the parameters of Black’s equation are specific for the studied material, and the results can be used for a comparison between layers with different fabrication processes.

A typical failure of a platinum stripe on oxidized silicon substrate after loading with a current density above 20 mA/μm² at a temperature above 650 °C for several hours is shown in Fig. 12. The failure occurred at the middle of the stripe (hottest area) and additional damage is visible on the stripe in its vicinity. This failure morphology indicates a behavior with void growth and not nucleation as the limiting

![XRD spectra around the platinum {100} peak measured for the pure-platinum test samples on a silicon chip before and after anneal in air and in N₂ atmospheres.](image)

![Specific electrical resistivities vs. temperature of 730 °C annealed platinum thin-film samples with different adhesion or mixed layers or SiO₂ passivation.](image)

![SEM image in topographical mode of a platinum stripe failure, showing a narrow interception in the middle along the length of a massively damaged stripe.](image)

![Cumulative distribution of the failure times of an electromigration experiment plotted together with the fitted cumulative and probability distribution functions.](image)
and improve their stability as already observed for aluminium addition inum grain boundaries, increase the activation energy of the samples lum adhesion layers, which lead to Ti or Ta oxide formation in the plat-grain boundaries and at the surface of the layer. The titanium or tanta-gestion that the electromigration-based damaging takes place in the distribution (Fig. 13).

The parameters of Black’s equation determined for different platinum layers are summarized in Table 1. A current exponent of ~2 has been determined for most of the tested material systems similar to the classical Black experiments [9]. The activation energies depend strongly on the fabrication process of the studied test samples. The value for the pure-Pt samples is, with 1.22 eV, low compared to the self-diffusion activation energy in bulk platinum of 2.89 eV [13], sug-gesting that the electromigration-based damaging takes place in the grain boundaries and at the surface of the layer. The titanium or tanta-lum adhesion layers, which lead to Ti or Ta oxide formation in the platin-um grain boundaries, increase the activation energy of the samples and improve their stability as already observed for aluminium addition to copper conductive lines [14]. An increase of the titanium content in the layer increases further the activation energy and improves the layer stability. The lift-off samples with Ti adhesion show a lower activa-tion energy compared to the corresponding etched samples, probably due to the minor edge quality as an effect of the fabrication process. The passivation of lift-off samples increased their lifetime by an order of magnitude, but also altered the failure mode, so that the parameters of Black’s equation cannot be compared to the other samples. Here, the failure occurred due to damage in the passivation by hillock forma-tion in the platinum stripe.

4. Conclusions

The test structures developed in this work are capable of measuring the thermal conductivity of insulating layers at temperatures of up to 400 °C with high precision. The measurements show that the different recipes for the PECVD SiO2 and the aging of the layers can strongly influ-ence the thermal conductivity, which need to be accounted for in the device design. The method is also capable of detecting adhesion defects at the platinum-oxide interface.

The diffusion of titanium and tantalum from the adhesion layer and of oxygen from the ambient atmosphere into the platinum do not only have an effect on the specific resistivity of the Pt layer but also improve the stability of the heater elements in terms of electromigration failure.

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