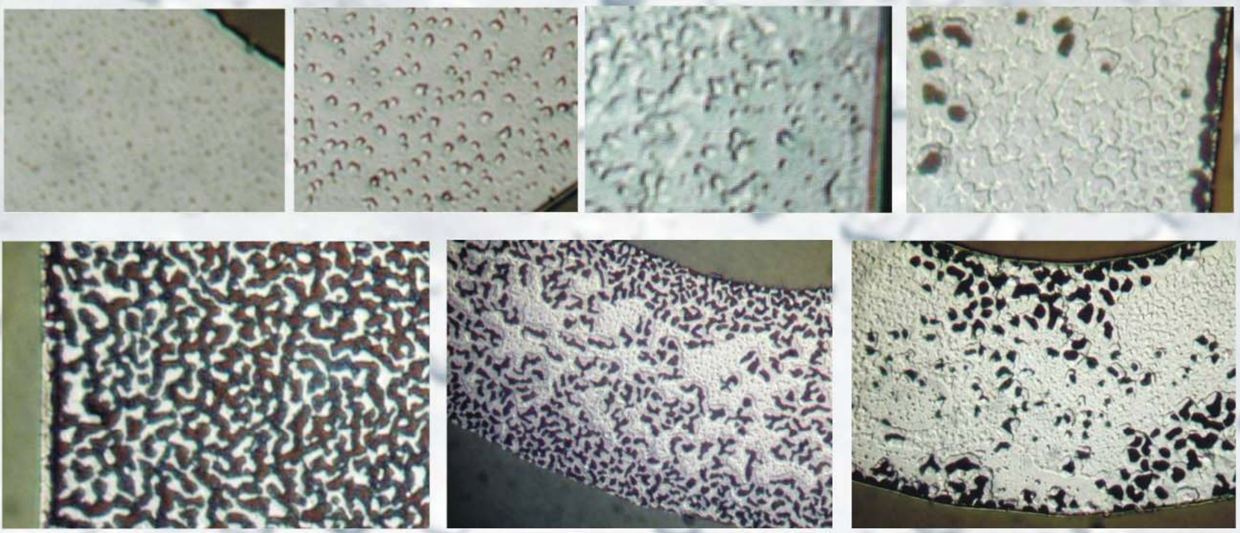
Degradation processes of platinum thin films on a silicon nitride surface



An Individual Research Assignment report (121013)

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Table of contents

0 Preface

At the end of the third year of the study of Electrical Engineering at the University of Twente, a project with a load of 240 hours of hard labour has to be done to put my engineering skills into practice. Because of my interest in clean-room stuff and my nice stay at the BIOS groups last year, I selected the TST group for doing my individual research assignment. After a nice email conversation with Roald Tiggelaar, I chose this assignment in the FORSIM project.

I really have had a wonderful time in the TST lab, doing this project. I'd like to thank Roald for his enthusiasm, support and educative comments. I think the good cooperation really raised the level of my research. I enjoyed the trips to the clean-room, when he spoiled another wafer I'd measured already. I also will remember the games of billiards very well (keep practicing Roald! ☺).

Further thanks go to Remco Sanders, a.k.a. Pino, for his help with the design and construction of the measurement setup and the measurements itself. Without him it was not possible to do the measurements on this small time scale.

And last but not least I'd like to thank Femke for her compliance in the weekend, when I was completely tired from working too intensively on my research project. I'll make it up to you in the holiday ☺.

Cheers!

Alfons Groenland

16-06-2004

1 Introduction

In the *FORSiM* project (***F****ast* ***O****xidation* ***R****eactions in* ***Si****licon-technology based* ***M****icroreactors*) silicon microreactors are developed suitable for executing (very) exothermic catalytic gas reactions. The reaction for which the microreactor is developed is the direct catalytic partial oxidation (CPO) of methane to synthesis gas. Synthesis gas is one of the most important intermediate products in the chemical industry and can also be used as ‘clean energy source’.

Due to the good thermic and mechanical properties of silicon it is possible to carry out chemical reactions in the so called ‘thin membrane microreactors’ that in the macroscopic world are involved with a great heat emission and therefore with explosion hazard. In these microreactors a number of heaters and temperature sensors are mounted to a thin membrane of ± 1 μm (figure 1). The heaters make sure that catalytic layer of rhodium gets the temperature required to starting the CPO reaction, while the temperature sensors measure the temperature of the gasses in the reaction channel (control of the reaction). A number of generations of microreactors are developed and tested, and by means of models the thermical and mechanical properties are partially examined

However, several issues in the field of the electrical properties as a function of temperature of the platinum heaters are not clear yet. In this individual research assignment (in Dutch: I.O.O.) these aspects are investigated. The problems concerning the platinum heaters are first theoretically considered in a literature study, theoretical solutions are considered to and finally practical solutions are implemented and verified by experiments.

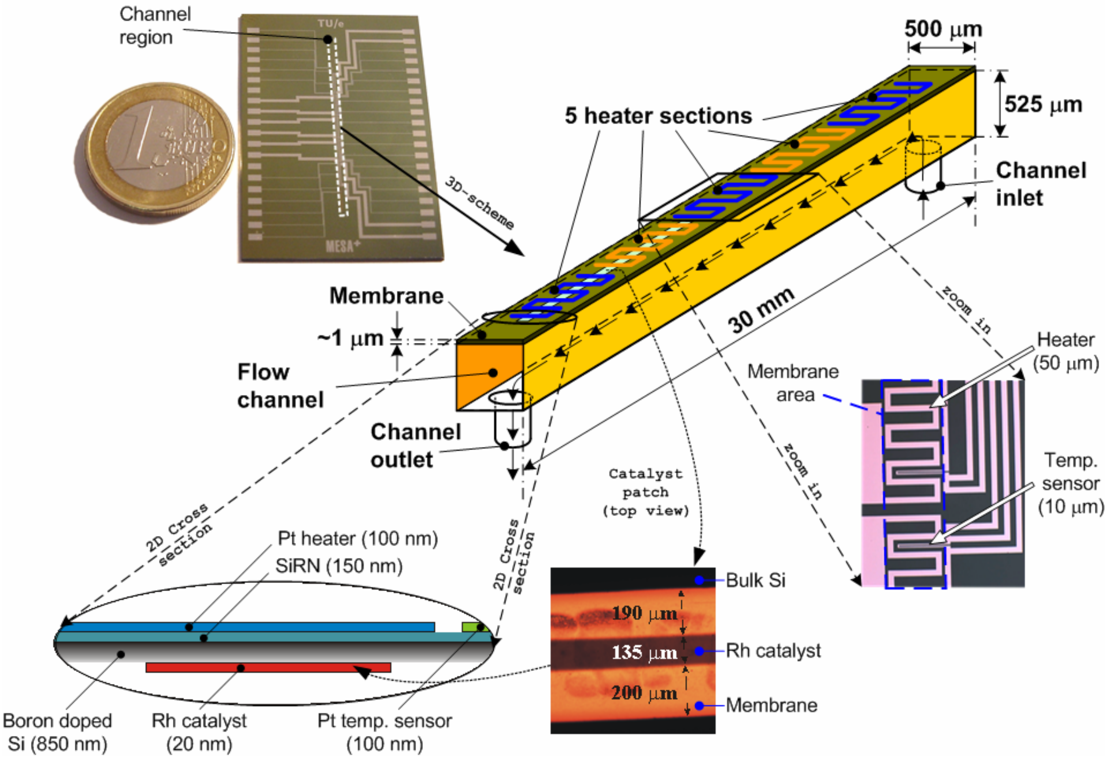

Figure 1 *Picture of the microreactor (3.0 × 4.5 × 0.1 cm^3) in which the flow channel region is marked. In the 3D-scheme the heater locations on the membrane are given. Close-ups of the membrane area with heaters and temperature sensors and the catalytic layer are shown as well as a 2D cross-sectional view of the channel, all with typecal dimentions (SiRN is low-stress silicon rich nitride).*

2 Theory

2.1 Electrical conduction in bulk metals

A solid piece of metal, at room temperature, consists of metal ions arranged in a regular pattern, called a crystal lattice, with free electrons moving in the spaces between the ions. The motion of the free electrons is random. The electrons have random thermal motion with an average speed of 10^2 km/s at 300 K. This is represented in figure 2a.

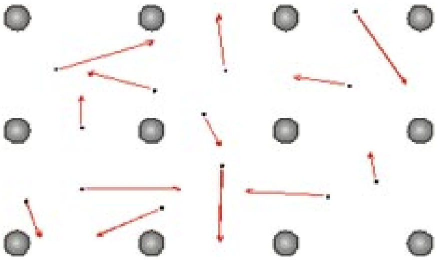

Figure 2a: movement of electrons in a piece of metal without a current flowing through it. The electrons only have thermal motion [1].

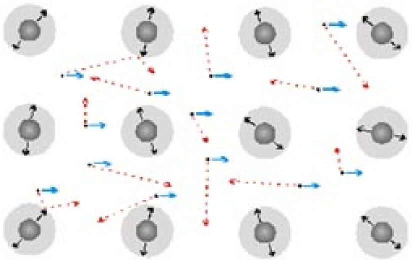

Figure 2b: movement of electrons in a piece of metal with a current through it. Right pointing arrows represent the drift velocity and the gray circles around the atom represent the lattice vibrations [1].

If the piece of metal is part of a circuit through which a current is flowing, then another motion is added to the random thermal motion. This motion is generally more in one direction and results in a general "drift" of electrons through the metal (for electrons in metals < 1 mm/s), as explained in figure 2b. The magnitude of the drift velocity depends on the current, the type of metal and the dimensions of the piece of metal [1]. In more detail, when an electric field $\mathbf{E}$ is applied to a piece of metal, a current density $\mathbf{j}$, proportional to $\mathbf{E}$ is induced in the metal with a length $\mathbf{L}$ (figure 3). This relation is known as Ohm's Law, $\mathbf{j} = \sigma\,\mathbf{E}$, with σ [Ω] the specific conductivity and $\rho = 1/\sigma$ [$1/\Omega$] the specific resistivity [2]. If electrons can move freely in the solid metal, a force applied to one electron by the electric field leads to an acceleration according to eq. 1:

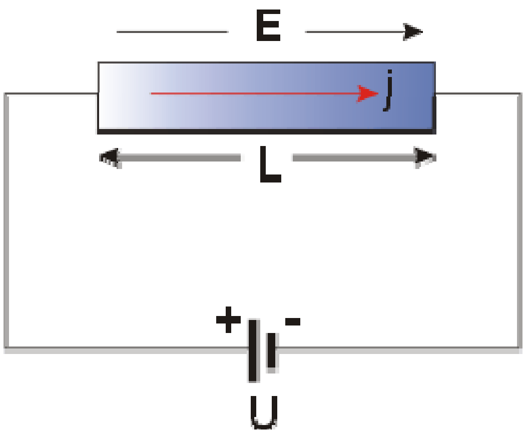

Figure 3 Model of a conducting piece of metal for deriving equations [2].

$$\mathbf{F} = -e\mathbf{E} = m\frac{d\mathbf{v}}{dt} \Rightarrow dv = -e\mathbf{E}dt \qquad \textbf{\textit{Eq. 1}}$$

Electrons however can't move freely through the metal because they sometimes collide with obstacles (like lattice vibrations/phonons or crystal defects). This is also called scattering and means the mean free path of the electrons is limited.

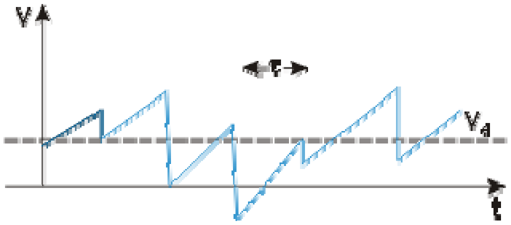

Figure 4 Example of the velocity of a single electron and definition of the average scattering time τ. [2].

This results in an average or drift velocity $\mathbf{v_d}$ which is related to the average scattering time τ (figure 4).

$$\mathbf{v_d} = -\frac{e\tau}{m}\mathbf{E} \qquad \textbf{\textit{Eq. 2}}$$

Applying this theory to classical particles with a charge $\mathbf{q}$, a mass $\mathbf{m}$ and a mobility μ, eq. 2 becomes:

$$\mathbf{v_d} = \mu\mathbf{E} = \frac{q\tau}{m}\mathbf{E} \qquad \textbf{\textit{Eq. 3}}$$

Using Ohm's law and $\mathbf{n}$ as the electron density, the specific conductivity (and thus the resistivity) can be derived with eq. 4, which is known as ***Drude's law***:

$$\sigma = \frac{ne^2}{m}\tau \Rightarrow \rho = \frac{m}{ne^2}\frac{1}{\tau} \qquad \textbf{\textit{Eq. 4}}$$

Since the scattering time τ is a function of the temperature (T), an expression for ρ can be derived, which is known as ***Mathiessen's rule***:

$$\frac{1}{\tau_{phonon}} = \begin{cases} \sim T^5 & \mathbf{T} < T_D \\ \sim T & \mathbf{T} \geq T_D \end{cases}$$

for the total scattering rate (number of collisions/second)

$$\frac{1}{\tau} = \frac{1}{\tau_{defect}} + \frac{1}{\tau_{phonon}} \Rightarrow \rho = \frac{m}{ne^2}\left(\frac{1}{\tau_{defect}} + \frac{1}{\tau_{phonon}}\right) \qquad \textbf{\textit{Eq. 5}}$$

T_D can be interpreted as the temperature from which the dependence of $1/\tau$ is not any longer proportional to T^5 but to T.

Interpreting Mathiessen's rule can lead to the argumentation that if temperature rises, electrons easier get from the valence band into the conduction band. The result would be that the resistivity of the metal decreases. However, experimentally the resistivity behaviour as shown in figure 5 is observed. This can be explained by the view that when temperature rises, the amplitude of lattice vibrations gets larger, which causes a smaller mean free path of the electrons in the conduction band or a shorter average scattering time τ. This is also explained in figure 6 in which several resistance curves are plotted as a function of the temperature. At low temperatures these curves are different because of the difference in purity (which is related to the number of crystal defects and the contamination of the metal) of the metals. It can be seen all curves converge to the same curve for higher temperatures.

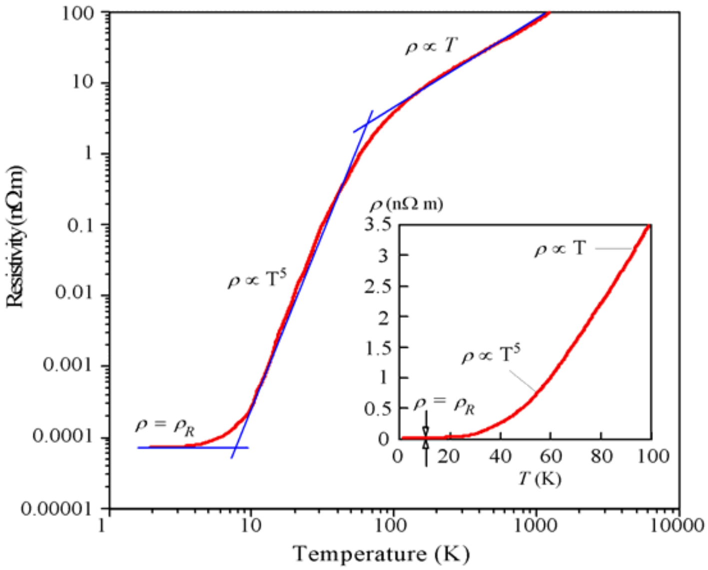

***Figure 5** The resistivity of copper from lowest to highest temperatures (near melting temperature,1358 K) on a log-log plot. Above about 100 K, when T=T_D of Eq. 5, $\rho \propto$ T, whereas at low temperatures, $\rho \propto T^5$ and at the lowest temperatures ρ approaches the residual resistivity ρ_R. The inset shows the shows the ρ vs. T behaviour below 100 K on a lineair (ρ_R is too small on this scale) [10].*

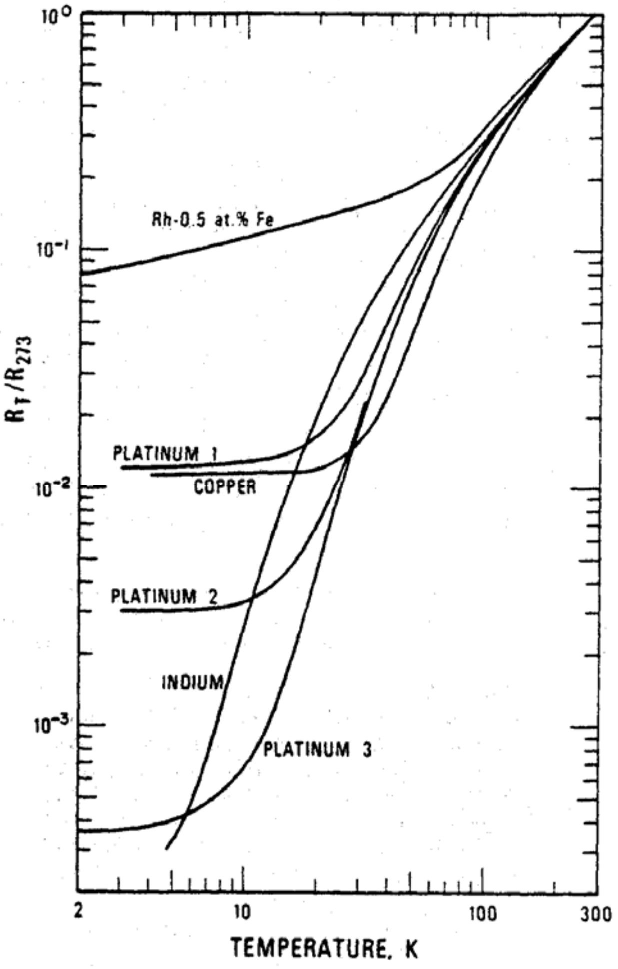

***Figure 6** Resistance ratio, R_T/R_{273} vs. temperature for copper, indium, Rh-0.5 at % Fe and platinum for three grades of purity [3]*

In this project, the resistivity of thin films of platinum is studied at temperatures greater than $\mathbf{T_D}$, so in this case $\rho \propto \mathbf{T}$.

During a collision of an electron with the crystal lattice, some of the kinetic energy possessed by the electron can be transferred to the ion. This makes the amplitude of the lattice vibrations increase further; the lattice was initially vibrating because of its temperature. This is also represented in figure 2b. Therefore, resistance to the current causes the temperature to increase or in other words, resistance causes electrical energy to be converted into thermal energy (internal energy).

2.2 Temperature coefficient of resistance

In fact, the dependence of the resistivity or the resistance can be described more accurately as mentioned in the previous chapter. A linear R(T)-relationship is related to a standard (reference) temperature (usually specified at 20 °C) and is described by [4]:

$$R(T) = R_0[1+\alpha(T-T_0)] \qquad \textbf{\textit{Eq. 6}}$$

$$R_0 = \rho\frac{l}{A} \qquad \textbf{\textit{Eq. 7}}$$

R = Conductor resistance at temperature “T” [Ω].
R_0 = Conductor resistance at reference temperature T_0 (20°C or 0°C) [Ω]
α = Temperature Coefficient of Resistance for the conductor material [1/°C]
T = Conductor temperature in degrees Celcius [°C]
T_0 = Reference temperature that α is specified at for the conductor material [°C]

The α is known as the temperature coefficient of resistance, and symbolizes the resistance change factor per degree of temperature change. Just as all materials have a certain specific resistance (at 20^o C), they also change resistance according to temperature by certain amounts. For pure metals, this coefficient is a positive number, meaning that resistance increases with increasing temperature. For semiconductors, this coefficient is a negative number, meaning that resistance decreases with increasing temperature. For some metal alloys, the temperature coefficient of resistance is very close to zero, thus when used for sensing it results in a sensor with a low sensitivity.

This α can be experimentally determined, but also analytically derived. According to Coutts, it can be written as:

$$\alpha = -\frac{e\varepsilon_0\varepsilon_r r}{4\pi k T^2} \qquad \textbf{\textit{Eq. 8}}$$

with **r** as the island radius which is proportional to the thickness of the thin metal film [5].

In fact, Eq. 6 can be considered as a linearization of a higher order function. In this view, the linear equation is the first part of the Taylor series of a higher order dependence between resistance and temperature.

$$R(T)\big|_{T=T0} = R_0(1+\alpha(T-T_0)+\beta(T-T_0)^2+\chi(T-T_0)^3+\delta(T-T_0)^4+\ldots) \qquad \textbf{\textit{Eq. 9}}$$

The sum of the first 4 powers of T is also called the **Callendar – Van Dusen Equation** which is used characterization of commercially available platinum temperature sensors [3][6].

2.3 Conduction in thin films of platinum

The shown theory in §2.2 describes the behaviour of the conduction for bulk metals. In this project however, thin films of metal are investigated. According to Erlebacher the conductivity (σ) is independent of thickness down to 100 nm, where as below 100 nm, the conductivity depends on the thickness. This means, when the thickness < 100 nm, the mean free path is determined by collisions with the film surface [7]. When the thickness > 100 nm, the conductivity is independent of the thickness.

In this project, the resistivity of thin layers of platinum is investigated. As concluded for bulk metals, the resistivity can be a linear function of the temperature up to a certain temperature. However, according to Firebaugh [8], this relation doesn't apply anymore for thin films of platinum at high temperatures. Thin films of platinum (100 nm) attached to a silicon-rich low stress nitride (SiRN) surface using a 10 nm titanium adhesion layer, degradate at high temperatures (500-1000 ºC). An example of degradation is displayed in figure 7. Due to this degradation, the resistance increases non-linear as a function of temperature.

A variety of degradation phenomena have been observed in thin films of platinum. These phenomena are significantly accelerated at elevated temperatures (T>500 °C). At lower temperatures these processes also occur, only at such a timescale they are hardly noticeable within a few hours of time [7]. In a chemical reactor temperatures can raise locally up to 1200 °C, so degradation effects can be noticed relatively fast (within tens of minutes).

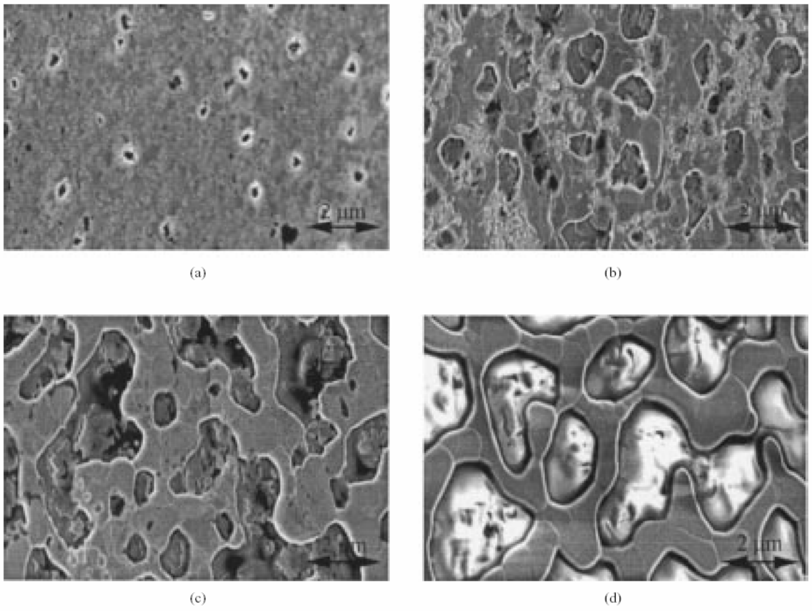

Figure 7 SEM images show the formation and growth of holes in the (10 nm/100 nm) Ti–Pt film.

(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 [11].

2.4 Degradation phenomena

According to Firebaugh, several degradation phenomena have been observed which can be responsible to a certain extent for the non-linear raise of the resistivity as a function of the temperature [5]. In summary, the reasons for degradation include interlayer diffusion and reaction, stress-induced morphological changes, electromigration, surface-driven and agglomeration.

2.4.1 Interlayer diffusion

Interlayer diffusion in thin platinum-titanium(Pt/Ti) bilayers deposited on top of silicon oxide (SiO_2) is observed after heating samples for 30 minutes at 600-800 °C. It is suggested Ti and oxygen (O_2) diffused through the grain boundaries of Pt and reacted with Ti until it was consumed completely. Because of the formation of several Ti-oxides, the top layer of Pt started to become bubbly and hillocks were formed. In this case the degradation of Pt is due to a chemical reaction of the Ti adhesion layer. These reactions decreased when platinum was deposited at high temperatures using a dc magnetron sputtering technique [12].

2.4.2 Stress-induced morphological changes

Another mechanism causing the Pt to bubble or to form hillocks are stress-induced morphological changes. The large thermal expansion mismatch between silicon nitride (1.6 ppm/K) and the Pt/Ti (8.8 ppm/K & 8.6 ppm/K respectively) might result in large compressive stresses at high temperatures, which the film can respectively relieve through hillock and hole formation. The hillock growth occurs as a result of differential relaxation rates between a grain in the polycrystalline film and its surroundings. This sets up a stress gradient which induces mass to flow along the substrate/film interface, pushing the relaxed area out at the base to form a hillock. For this reason, tantalum (Ta) is preferred as an adhesion layer, because its thermal expansion coefficient of 6.3 ppm/K. This might reduce the stress in the Pt by creating a graded change in expansion coefficient. Furthermore Ta is much less reactive as titanium or chromium. For this reason, tantalum is used in this project as adhesion layer between silicon-rich nitride (SiRN) and Pt.

2.4.3 Electromigration

Another phenomenon to consider is electromigration, mass flow driven by the interaction between the atoms of conductor and the direct current of electrons flowing through it. Electromigration typically occurs in thin films when high current densities (10^5 to 10^7 A/cm^2) are present at moderate temperatures relative to the material melting point ($0.3\ T_m < T < 0.7\ T_m$). In this project, working temperatures are 10% - 60% (locally) of the melting temperature of platinum ($T_{m,Pt}$=1768 ºC [13]). Current densities however used in this project for heating (± 10^3 A/cm^2) are however, below 10^5 A/cm^2, so this phenomenon can be considered as less significant. This is confirmed in literature by Srinivasan by who's comparable experiments still no electromigration occurs in thin platinum films at a current density of 9 10^6 A/cm^2 [14].

2.4.4 Recrystallisation

The fourth main effect is recrystallisation. This effect is observed in both bulk as thin films of platinum [15][16]. Bulk platinum, as deposited, is not highly structured. When the platinum is heated, the atoms start to reorder in such a way that the energy state will decrease by the formation of crystals. This brings about that the number of grain boundaries decreases thus a reduction of the resistance. In thin films, however, the formation of these crystals is limited by the thickness of the film. Therefore atoms needed for the formation of crystals come from the material among the crystal nuclei, causing the film to degrade into separate electrically isolated hillocks. In this case the resistance increases dramatically, until this films is converted into a collection of complete separate islands. The resistance is in this case approaching infinity. According to our knowledge, Firebaugh describes this recrystallisation in thin films with the term ‘agglomeration’ [8].

2.4.5 Agglomeration

Agglomeration is driven by the high surface to volume ratio of thin films. Surface diffusivity, which is exponentially dependent on temperature, acts to reduce the surface area through capillarity. The process is a nucleation and growth process. Defects, pinholes or thermal grooving at a grain boundary must first establish a hole greater that a critical radius, which is determined by the film thickness and wetting angle. Stress can hasten the formation of a hole by differentially thinning the material. Once the critical radius is achieved, the hole will grow until the film is transformed into a collection of unconnected, hemispherical islands which are electrically isolated.

2.5 Improvements for obtaining high temperature stability

The degradation process as described in the last section is undesirable when platinum is used for heaters in microreactors. As already mentioned, this process also takes place at room temperature and is accelerated by high temperatures, so the solutions to this process aim at the delay of the process [9].

According to Alépée, there are several ways to improve the high-temperature stability of Pt thin films [16].

- Stabilizing the layers by annealing
- Increasing the layers thickness
- Alloying platinum with high melting point materials
- Passivating the layer with a dielectric thin film
- Depositing platinum without an adhesion layer

2.5.1 Stabilizing the layers by annealing

The first method is annealing. Alépée tested structures of silicon nitride (Si_3N_4), with a 200 nm thin film of platinum (Pt) on top. The platinum film was attached to the surface using an adhesion layer of 10 nm tantalum (Ta). Before exposing the samples to high temperatures on which the degradation effects occur fast (1 hour @ $T \geq 800$ °C), the samples are annealed in a furnace up to 650 °C for 2 hours. The effect of this annealing is that the platinum starts to degrade softly. After annealing the platinum film is not as smooth as before, but when subsequently heated up to the degradation temperature, it degrades not any further. Alépée determined the optimal annealing temperature had to be 650 °C. Samples annealed at 550 °C behaved the same as non annealed samples.

Annealing seems to be an efficient way of stabilizing platinum thin films by a soft recrystallisation. However, platinum is an excellent catalyst for numerous reactions, which can take place during annealing. These reactions will disturb a neat crystal formation. This can be solved by a passivation layer onto the Pt-Ta layer which will be explained in § 2.5.4. As will be seen, without passivation of Pt, annealing is hardly useful for extending the lifetime by powers of 10. Another disadvantage of this annealing method is that thermal stability is only investigated for temperatures up to 1000 °C. In this project, temperatures can increase locally up to more than 1200 °C, due to active heating in a combination which crystal defects. Annealing does not guarantee thermal stability at these very high temperatures.

2.5.2 Increasing the layer thickness

Increasing the layer thickness of platinum with respect to the adhesion layer reduces the surface to volume ratio and therefore recrystallisation or agglomeration is seriously reduced. Firebaugh observed that the lifetime of a 400 nm thin platinum film compared to a 200 nm thin film increased by a factor 3, so it is clear a thicker film increases the thermal stability [8]. A factor 3 for this project is nice, but the ambition is a longer extension of the lifetime so increasing the thickness of the platinum layer can be considered a partial solution.

However, when passivating a thin Pt layer, it is easier to ‘cover’ a thin layer than a thick layer. This means problems can occur during passivation like coverage problems and stress problems.

2.5.3 Alloying platinum with high melting point metals

Alloying platinum with high melting point metals like iridium, tungsten or rhodium would give an alloy with a melting point between the melting points of platinum and the other metal. This is true, on the condition that the two metals do not form an eutectic. Another boundary is that the resistivity of the alloy is of the appropriate order. This can be an interesting solution, however it is very difficult to deposit a nice, thin and homogenous layer of an alloy of the right mixture of the two metals. Using the present deposition techniques, this is not possible yet in a way its applicable in this project.

Alloys often have a low TCR (α) which is not desirable for application as an replacement for Pt in temperature sensors. Although Pt in this project is used for heating purposes, another application in the microreactor is temperature sensing. If sensing requires a high α and the same material and process is used for creating both sensors and heaters, using an alloy is not an option. Of course 2 different materials can be used for both purposes, but then more process steps are introduced to the fabrication process of the microreactor. This is undesirable because of the increasing potential fabrication faults.

2.5.4 Passivation

Passivation is an interesting way of protecting the platinum from malignant influences that can cause degradation. Passivation means that a protecting layer of another material is put on top of the thin platinum film, sealing the platinum. Passivation has two major advantages:

1) Pt can not make contact to reactive gases (like O_2) that can cause Pt to degrade. Therefore, the passivation layer has to be gas-tight (pin-hole free) to ensure that reactants can not diffuse through the platinum layer.

2) Passivation can fix the platinum mechanically. Mechanically caused degradation effects like stress-induced morphological changes and surface-driven agglomeration can be competed. By fixing the platinum both bottom and top side, it's more difficult for platinum atoms to rearrange. Note that the passivation layer has to be an electrical insulator.

Both advantages induce however difficulties in passivating thin platinum films. Alépée investigated the passivation of thin platinum film in four different ways:

1) Passivation the Pt by depositing a 140 nm thin layer of LPCVD Si_3N_4. It is possible to create a thin pinhole-free layer on the Pt. However, this LPCVD process takes place at 770 °C and at this temperature the Pt already starts degrading while putting on the protecting layer.

2) Depositing a pre-encapsulation layer of 200 nm aluminium oxide (Al_2O_3) at room temperature, which is used to prevent the Pt from degradation at higher temperatures when a 140 nm thin layer of LPCVD Si_3N_4 is deposited. However, degradation still occurs because the Al_2O_3 layer contained too many pinholes and did not encapsulate the platinum at all.

3) Deposit Si_3N_4 by a PECVD process. This process is done at lower temperatures (T ± 300 °C). The problem that occurred in this case was that after annealing the sample for 1 hour @ 800 °C the Pt also degraded, due to chemical reaction that took place involving the Pt. The passivation layer was not chemical

stable. The PECVD Si_3N_4 is H_2 rich (20-25%) and Pt is an excellent catalyst for the hydrogen combustion at high temperatures ($H_2 + ½ O_2 \rightarrow H_2O$). This means, if oxygen can diffuse through the passivation layer at the same time as the nitride degasses, the extremely exothermic combustion reaction will take place at the Pt surface using it as a catalyst and deteriorating it. By depositing a 300 nm layer of PECVD Si_3N_4, which is done in own experiments, passivation failed because of stress problems, causing this solution to be mechanically unstable.

4) Putting a layer of silicon carbide (SiC) on top of it. SiC is a semiconductor in the crystalline state, but in the amorphous state it is a dielectric. Due to deposition problems, the film deposited by RF magnetron sputtering turned out be not amorphous enough so started conduction.

Therefore can be concluded Sic is both chemically and mechanically stable, but not electrically insulating so also unusable.

2.5.5 Conclusions

All solutions to reduce degradation of thin platinum films as mentioned before, were about platinum (Pt) films, attached to silicon-nitride using an adhesion layer of 10 nm tantalum (Ta) / titanium (Ti). Both Pt and Ta are conductors with approximately the same resistivity [ρ_{pt} 10.6 /10^{-8} Ω m, ρ_{ta} 13 /10^{-8} Ω m [13]] so approximately conduction takes place in a film with the thickness the sum of both layers. Oxidation of the adhesion layer occurs because of pinholes in the Pt film and therefore reduces the amount of material participating in conduction, causing the resistivity to increase and deteriorating the adhesion of the Pt to the silicon-nitride. According to Alépée this influence in the resistivity is negligible [16]. However, the formation of tantalum oxides and other reaction products can induce stress in the layers, and because of this stress other degradation mechanisms can be accelerated. To eliminate the contribution of the adhesion layer to the degration of thin platinum films, platinum can be deposited without an adhesion layer. This is, however, non trivial due to adhesion problems of Pt on to silicon-nitride, but due to new technological developments this is a possibility at the moment. By depositing platinum directly on the silicon-nitride, interlayer reaction and reaction and stress-induced morphological changes can be decreased.

2.6 Conclusions of the theory

The non-ideal behaviour of the resistivity of thin platinum films as a function of the temperature is due to degradation effects that are accelerated by high temperatures. 100 nm thin platinum films adhered to a silicon-nitride surface using an adhesion layer (of 10 nm tantalum or titanium) suffered from degradation. Several degradation effects are considered and they all contribute more or less to the degradation of platinum. In the circumstances the platinum is in this project, the main effects are interlayer diffusion and reaction, stress-induced morphological changes and recrystallisation or surface-driven agglomeration. They all result in the main effect that the homogenous platinum film mutates to a non-homogenous collection of separate beads causing the resistivity to increase non-linear. Electromigration is considered too, but is considered not significant because the required high current densities are not present.

Several solutions to reduce degradation and hence increase the lifetime of the microreactor are considered. The main solutions seem stabilizing the layer by annealing, increasing the layer thickness of platinum, passivation of the platinum layer with a dielectric thin film and (or in combination) depositing platinum without an adhesion layer. They all contribute in a positive way to the delay of the degradation process.

Annealing provides thermal stability of the film only up to the annealing temperature. Increasing the film thickness from 100 nm to 200 nm delays the lifetime of the film by a factor 3. Passivation looks promising but the production of a chemically and mechanically stable, non-conductive passivation film has not been demonstrated without affecting the platinum during the deposition of the platinum layer. Depositing platinum without an adhesion layer can delay interlayer reaction and stress-induced morphological changes, but due to technological imperfections, it has not been experimentally proven yet. Alloying platinum with high melting point materials looks promising, but it is at this time still very difficult so deposit a nice, thin and homogenous layer of an alloy of the right mixture of the two metals. In summary, none of the separate methods provide a satisfactory solution.

3 Experimental

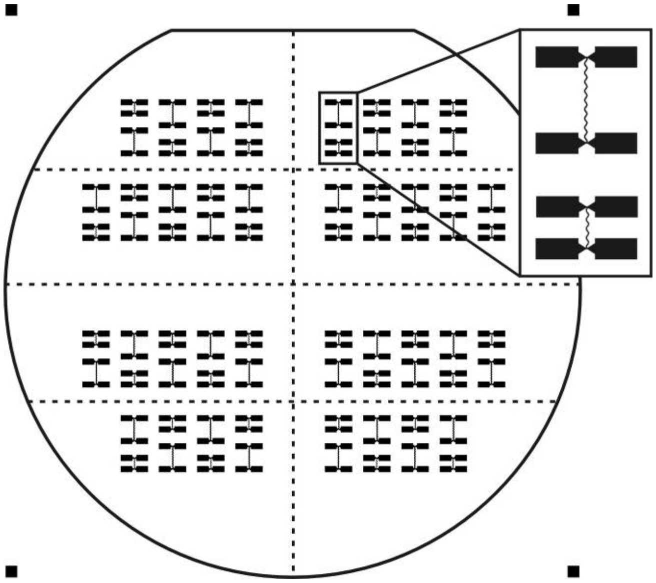

Figure 8a: Layout of the test wafer with sinusoidal shaped heaters of 2 lengths with contact pads. Each wafer is devided in 8 pieces. In measurement , only one group of four test structures (two small and two large ones) is used.

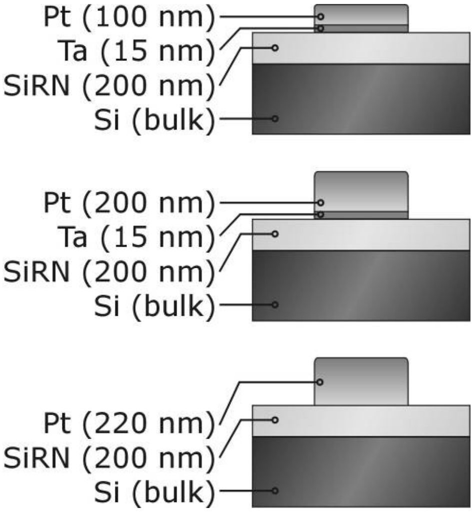

Figure 8b: Composition of the three different wafers: 100 nm Pt with Ta adhesion layer, 200 nm Pt with Ta adhesion layer and 220 nm Pt without adhesion layer.

In this project a number of solutions to increase the high temperature stability of thin platinum films are tested. The influence of stabilizing the layers by annealing, increasing the layer thickness and depositing platinum without an adhesion layer are tested. The purposes of this investigation were to gain knowledge about the different degradation phenomena as well as the adhesive properties of Pt-thin films as function of annealing conditions.

Heater structures of Ta/Pt and Pt were fabricated to test the high-temperature behavior of these metal-films (figure 8). Two structures were used during the experiments: the dimensions of the first structure were identical to the sinusiodal heaters used in the FORSiM-microreactors [17]: the length of the sinusoidal shaped wire was 4.6 mm and the width of the wire 50 µm. The second structure was identical to the first structure, except that its length was 2.3 mm instead of 4.6 mm. After deposition of ~200 nm LPCVD SiRN on 525 µm thick (100)-oriented p-type silicon (100 mm), different procedures were applied to deposit Ta/Pt or Pt.

3.1 Ta/Pt films

With standard lithography the pattern of the heater structures is defined in a resist layer. Subsequently, layers of Ta (15 nm) and Pt (100 nm or 200 nm) are sputter-deposited on this layer. Ultrasonically enhanced lift-off in acetone is used to dissolve the resist layer. Cleaning steps in ethanol and DI-water are performed after lift-off, and finally the wafer is spin-dried. The pattern of Ta/Pt heaters after removal of the resist (and thus also the metal thin-film on the resist) is shown in figure 8.

3.2 Pt films

Prior to sputter-deposition of a layer of Pt (~220 nm), the SiRN-layer is exposed to an SF_6/O_2-plasma for 1¾ minutes (6:1-ratio; pressure: 40 mTorr, P: 60 W). This plasma removes contaminations and (possibly) slightly roughness the SiRN-surface. With standard lithography the pattern of the heater structures is defined in a resist layer. With an O_2-plasma the exposed Pt is passivated with a thin oxide layer (pressure: 10 mTorr, P: 60 W; time: 1 min.), whereas the Pt covered by the resistlayer is not passivated. When the acetone is removed (with acetone), the colour of exposed Pt changes from grey into yellowish. The unexposed Pt is then etched away in a mixture of H_2O, HCl and HNO_3 (H_2O:HCl:HNO_3(69 %)-ratio = 8:7:1), leaving well-adhesive and well-defined Pt structures. The etchrate of Pt in this mixture highly depends on the temperature. However, at 90 °C ± 1 °C a layer of ~220 nm unexposed Pt is removed completely within 2 minutes. Finally, the substrate is cleaned in ethanol and DI-water and is spin-dried. The etchrate of O_2-passivated Pt is indeed highly retarded [18]: no etching of the exposed Pt can be detected height measurements.

Finally the wafers with the Ta/Pt and Pt structures were divided into 8 separate parts (samples).

Table 1 Anneal temperatures used in own experiments

$T_{anneal\ I}$ [°C]	250	450	550	650	750	850	950	750
Ramp up speed [°C/min]	10	10	10	10	10	10	10	5
$T_{anneal\ 2}$ [°C]	1000	850	650					
Ramp up speed [°C/min]	10	10	10					

Samples were annealed at temperatures, based on experiments by Alépée [16] and as mentioned in table 1. Annealing was done at the temperatures for one hour and with a ramp up of 10 °C/min and an evenly cool down to prevent the samples from breaking because of thermally induced stress problems. Annealing is done in air ambient. To determine the influence of the ramp up speed, three samples with different layer compositions were annealed with a ramp up speed of 5 °C/min. Before annealing, the resistance of the samples was measured.

After the first annealing run, some samples were annealed a second time to study the influence of this 'two step' annealing.

Because the resistance is a linear function of the temperature, R0 and the TCR are measured at [20-60 °C] (for time saving reasons, only for increasing temperatures). To verify this assumption, the TCR and R0 of three samples of different sample types were measured at [20-325°C]. Also for one sample the resistance as a function of the temperature was measured during the cooling down to verify that no hysteresis of the resistance occured. Both R0 and the TCR are determined by looking at a linear fit through the data series of the resistance as a function of the temperature. R0 is an extrapolated value of this R(T)-curve at 0 °C which can be calculated for every data series the same way.

4 Measurement setup

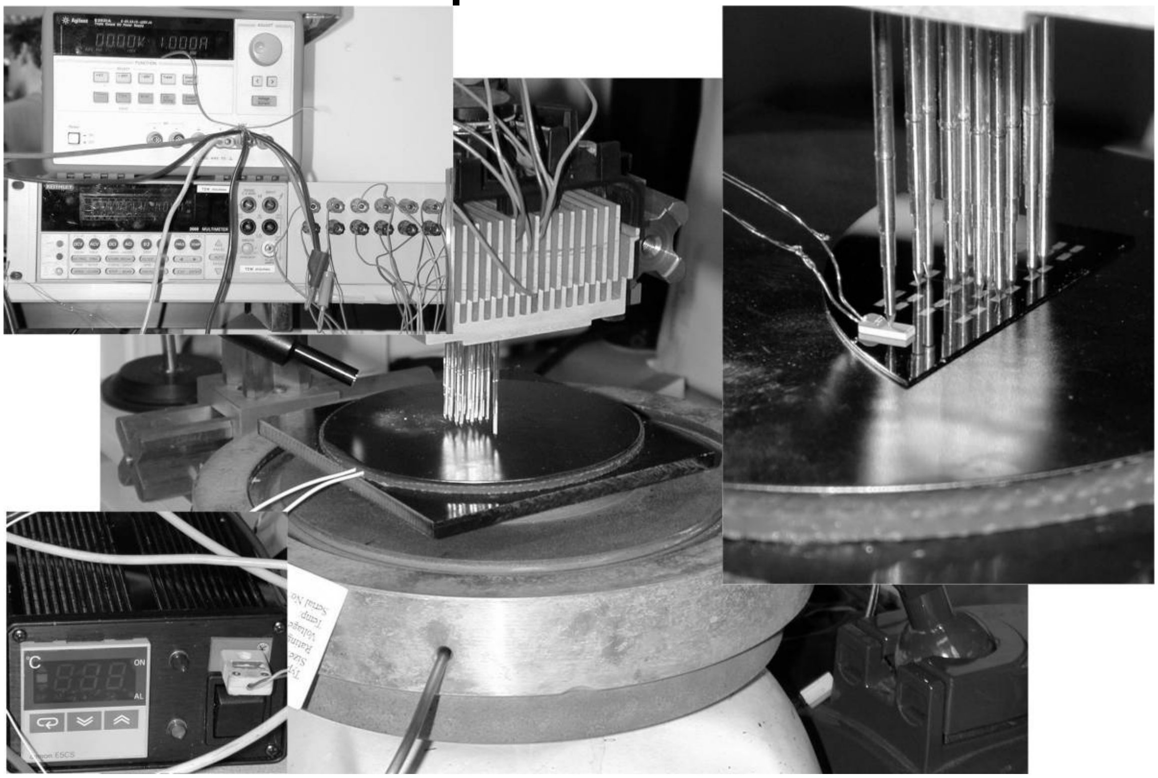

Figure 9: Measurement setup with the hotplate, on top a mica plate with the small heater covered by the heat conducting wafer. Details: top left: the Agilent E3631A power supply and the Keithley 2000 multimeter. Top right: small heater with the heat conducting wafer and a sample with test structures. Four test structures are measured simultaneously using 16 sharp suspended pointed probes to minimize the heat leakage through the probes. In front of the probe array the small thin film PT100 element used for temperature sensing on the wafer. Bottom right: the manual operated temperature controller for the hotplate.

R0 and the TCR of one sample are determined by measuring the resistance of four test structures parallel during heating from 20 to 60 °C at ± 4°C/min. Resistances have been measured in a 4-point configuration to minimize the influence of the contact wires, using a Keithley 2000 multimeter. Heating is done using a small external heating element (Jimi~Heat JMS/EB 17C), whose power is precisely controlled by an Agilent E3631A programmable DC power supply. The small heater is covered by a bare silicon wafer for optimal heat conduction to the sample. The temperature of the wafer is measured using a commercially available thin film PT100 temperature sensor. The output voltage of this PT100 is measured in a four point configuration using a HP 34401A multimeter. Thin wires are used to minimize the heat leakage by the contact wires. All equipment is controlled using a HPVEE program.

For the determination of R0 and the TCR for the temperature range of 20-325°C the hotplate was used instead of the small heater. This upper temperature was limited by the measurement setup: just below the melting point of the used high temperature solder. The small heater and mica plate were removed and the test sample with heat conducting wafer was placed directly in top of the hotplate. The temperature of the hotplate was controlled manually, while the HPVEE program logged the resistance of the thin platinum film structures.

Height-profiles of the thin platinum film are determined by a surface profile measurement using a Veeco Dektak 8 before and after annealing. Heights are the average of the surface profile. The roughness of a surface is determined by the visual examination of the surface profile.

Pictures of the samples are made with a Leitz microscope in combination with a Nikon CoolPix 950 digital camera (positioned in the oculair).

The adhesion strength of the thin-films was tested using the well-known Scotch-tape test [19]: all films after every anneal treatment passed this test.

5 Results

The electrical properties of annealed samples like the TRC and R0 are determined, as well as the physical properties like the height and the morphology of the film. In every section, the measurements are divided in into two parts: the ‘basic’ results and the ‘special’ results. In the basic section, samples are discussed, all annealed the same way with different anneal temperatures. In the special part, the other measurements like the two step annealing are discussed.

5.1.1 Electrical analysis: basic results

First the basic results are discussed, subsequently the other results. The results of the R0 and TCR are displayed in figure 10 and discussed in § 5.1.1-5.1.2.

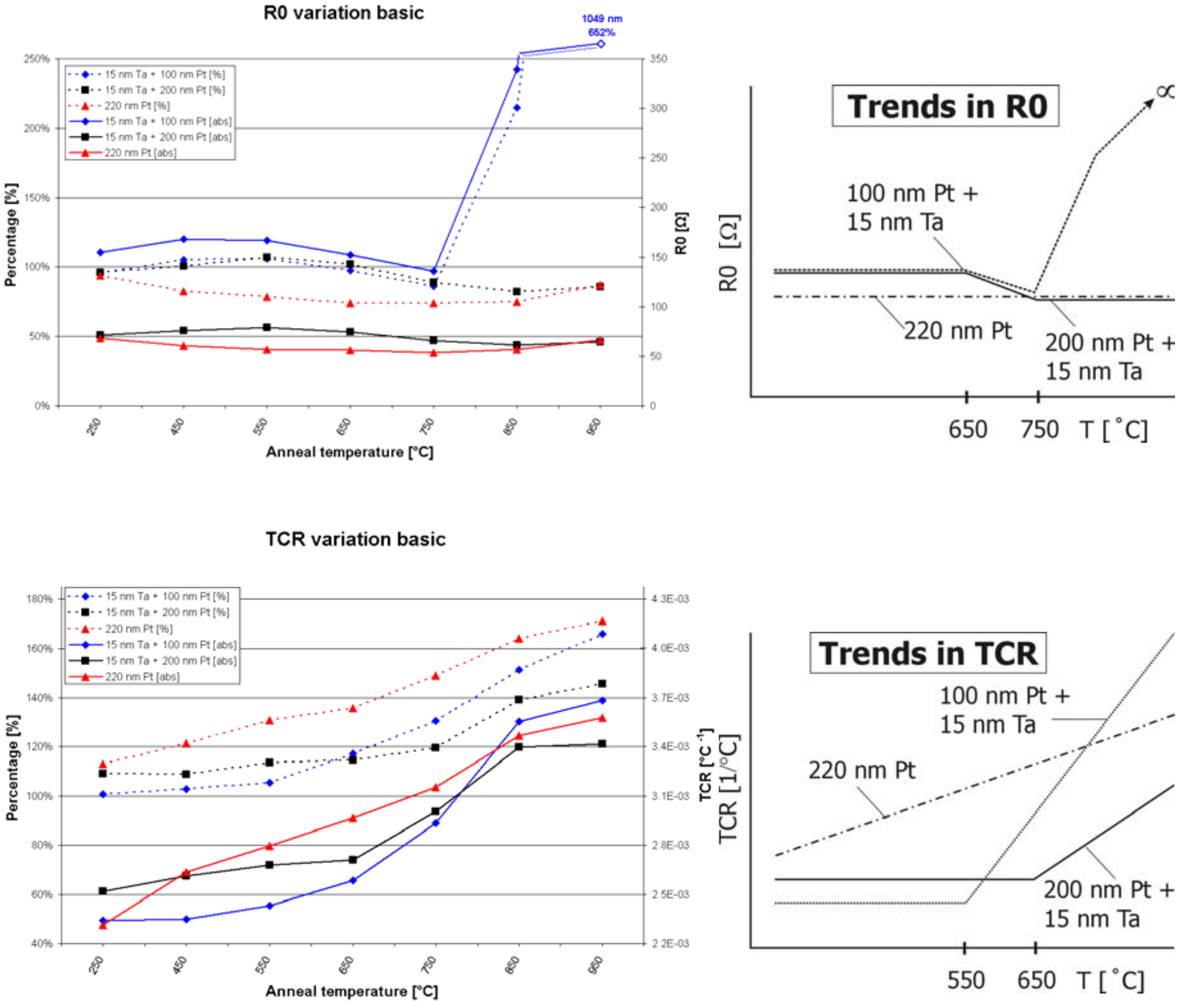

Figure 10 Basic results of the electrical analysis. R0 and TCR as a function of the anneal temperature (ramp up speed 10 °C/min, hold time 1 hour, passive cool down) for several layer compositions. Right hand side: trends in R0/TCR.

5.1.1.1 Basic: R0 and the TCR, one step annealing @ 10 °C/min

15/100 nm Ta/Pt and 15/200 nm Ta/Pt

R0 is constant up for anneal temperatures up to 650 °C, for both layer thicknesses, roughly as ±$R0_{initial}$. For anneal temperatures above 650 °C, R0 for 15/100 nm Ta/Pt increases very strongly. No clear relation between R0 and the anneal temperature can be derived. This is because of the severe degradation of the 15/100 nm Ta/Pt film. R0 for 15/200 nm Ta/Pt above 650 °C can considered a constant, ±0.8*$R0_{initial}$. This is illustrated in figure 10.

The stability of the TCR depends of the layer thickness: 15/100 nm Ta/Pt is constant up to including 550 °C and for higher anneal temperatures linear with the anneal temperature. 15/200 nm Ta/Pt is constant up to including 650 °C, for higher anneal temperatures the TCR is a linear function of the anneal temperature.

5.1.1.2 Basic: R0 and the TCR one step annealing @ 10 °C/min

220 nm Pt

R0 is almost constant for anneal temperatures of 450-1000 °C, at ±0.8*$R0_{initial}$.

The TCR increases linearly for anneal temperatures of 450-1000 °C. The absolute value of the TCR can be derived as in eq 10.

$$\alpha(T) = 0.0002T + 0.022 \qquad \textbf{Eq. 10}$$

5.1.1.3 Basic: conclusion on basis of the electrical properties

Both 15/200 nm Ta/PT and 220 nm Pt are on basis of these electrical properties the best choice for implementation in the microreactor, because of the stability at higher anneal temperatures. Although the relations for R0 and the TCR for both thick layers differ as a function of the anneal temperature, they both are clearly determined. 15/100 nm Ta Pt is not useful for implementation in the microreactor because of its instability of R0 at anneal temperatures of 950 °C and above.

5.1.2 Electrical analysis: other results

The results of the other measurements together with the basic results are displayed in figure 11 and discussed in § 5.1.2.1-5.1.2.4. .

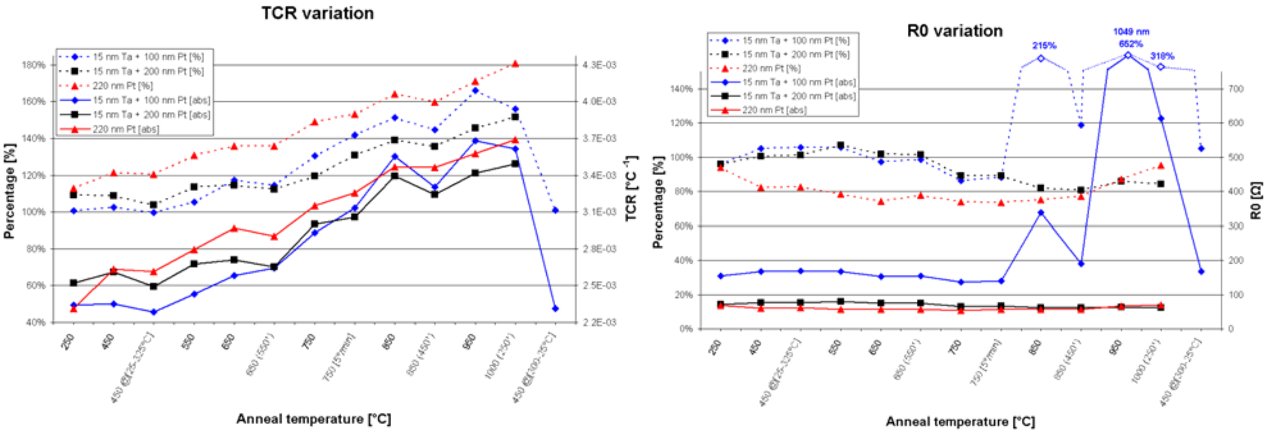

*Figure 11: Other results: all results of all measurements summarized, including the basic results.
Left: TCR, right: R0.*

5.1.2.1 *R0 and the TCR for measurements at [20-325 °C]*

15/100 nm Ta/Pt, 15/200 nm Ta/Pt and 220 nm Pt

R0 and the TCR are also determined at [20-325 °C]. This is done to verify if R0 and the TCR determined at [20-60°C] are the same as determined for higher temperatures. If both R0 and the TCR are the same for both methods, heaters/sensors in practical use can be calibrated on the low temperature range, which is preferable. The results are summarized in table 2 and in figure 11.

Table 2 Comparison of the determination of the TCR and R0 at measurement temperatures of [20-60 °C] and [20-325 °C].

Structure	T_{anneal} [°C]	R0 [Ω]	TCR [1/°C]	R0 [Ω]	TCR [1/°C]	Δ R0 [Ω]	**Δ R0 [Ω]**	Δ TCR [1/°C]	**Δ TCR [1/°C]**
		T[20-60°C]	T[20-60°C]	T[20-325°C]	T[20-325°C]	Abs	**%**	Abs	**%**
100 nm Pt / 15 nm Ta	450	167.834	2.35E-03	168.891	2.29E-03	1.057	**0.63%**	6.50E-05	**2.76%**
200 nm Pt / 15 nm Ta	450	75.995	2.62E-03	76.505	2.50E-03	0.51	**0.67%**	1.20E-04	**4.59%**
220 nm Pt	450	60.823	2.64E-03	61.091	2.61E-03	0.268	**0.44%**	2.69E-05	**1.02%**

The difference in R0 is < 1%, so not significant. The difference in the determinations of the TCR is 1-5% and depends on the layer composition and thickness. Based on these results above, it can be concluded that the TCR can be determined over [20-60°C] with an uncertainty < 5%.

5.1.2.1 *R0 and the TCR for measurement at [20-325 °C] and [325-20 °C]*

15/100 nm Ta/Pt, 15/200 nm Ta/Pt and 220 nm Pt

To be sure no hysteresis occurs when measuring the TCR and R0 for only increasing temperatures, of one sample the R(T)-curve is measured during cooling down. From R(T)-measurements during heat up and cool down, R0 and the TCR are determined and compared. This is done in table 3.

Table 3 Comparison of the determination of the TCR and R0 for an increasing and decreasing measurement temperature.

Structure	T_{anneal} [°C]	R0 [Ω]	TCR [1/°C]	R0 [Ω]	TCR [1/°C]	Δ R0 [Ω]	**Δ R0 [Ω]**	Δ TCR [1/°C]	**Δ TCR [1/°C]**
		T[20-325°C]	T[20-325°C]	T[325-20°C]	T[325-20°C]	Abs	**%**	Abs	**%**
100 nm Pt / 15 nm Ta	450	168.99	2.29E-03	168.31	2.31E-03	0.67723	**0.40%**	2.61E-05	**1.14%**

It can be concluded that the difference in R0 and the TCR are in the range of 1%, therefore no hysteresis in the TCR and R0 has to be taken into account.

5.1.2.3 *R0 and the TCR for annealing with different ramp up speeds*

15/100 nm Ta/Pt, 15/200 nm Ta/Pt and 220 nm Pt

To study the influence of the ramp up speed to the degradation of the thin platinum film at one anneal temperature, 2 samples with the same layer composition were annealed at the same temperature (750 °C), but with different ramp up speeds of 5 °C/min and 10 °C/min.

According to figure 11, it can be concluded the change in R0 of a sample annealed at 5 °C/min is almost the same to the change in R0 of a sample annealed at 10 °C/min.

The TCR of the sample annealed with 5 °C/min is however higher than the TCR of a sample annealed at 10 °C/min. In more detail, this the TCR and R0 at 5 °C/min are nicely on the curve between the the TCR's/R0's of samples annealed at 750 °C and 850 °C with ramp up speeds of 10 °C/min. This indicates the platinum film of the sample annealed with 5 °C/min degraded more then the sample annealed at 750 °C with 5 °C/min, but less then the sample annealed at 850 °C with 10 °C/min.

Therefore, it can be concluded that the ramp up speed during annealing is definitely a major parameter in the degradation of thin platinum films, independent of the three layer compositions, but it's influence has to be studied further to say more detailed things about it.

5.1.2.4 R0 and the TCR for annealing at two different temperatures for one sample (2-step)

15/100 nm Ta/Pt, 15/200 nm Ta/Pt and 220 nm Pt

To study the influence of a second anneal treatment applied on to earlier annealed sample, several samples are annealed this way. This means samples are annealed at one temperature, cooled down and after measurement of the resistance (as a function of the temperature) these samples are annealed a second time. The results of these experiments are illustrated in figure 11 labelled as 650 (550^1) °C, 850 (450^1) °C and 1000 (250^1) °C.

R0 and the TCR of the 650 (550^1) °C and the 850 (450^1) °C samples are compared to R0 and the TCR of samples annealed at 650 °C and 850 °C in one step.

R0 of samples annealed at 650 °C and 650 (550^1) °C are approximately equal for all three layer compositions. R0 of 15/200 nm Ta/Pt and 220 nm Pt are approximately equal for both samples annealed at 850 °C and 850 (450^1) °C, while R0 of 15/100 nm Ta/Pt decreases dramatically for the two-step sample.

The TCR seems to be for the sample of 650 (550^1) °C slightly lower. This indicates the two-step annealed sample is less degraded in comparison to the one step sample, independent of the layer composition. The TCR of the two-step sample is considerable lower than the TCR of the one step sample, independent of the layer composition.

On basis of the difference in the TCR, it could be concluded the thin platinum film of the two-step sample has the same degradation level compared to the one-step sample for all three layer compositions. However, on basis of the change in R0, this only holds for the 15/200 nm Ta/Pt and 200 nm Pt samples. Because of the dramatic decrease of R0 of the 15/100 nm Ta/Pt sample, it can be concluded this sample is less degraded in comparison to the one step sample. The two-step anneal treatment only has a positive effect on the 15/100 nm Ta/Pt sample, no difference can be noticed for both 15/200 nm Ta/Pt and 220 nm Pt samples.

The 1000 (250^1) °C sample can be compared best to the sample annealed at 950 °C in one step, assuming the influence of the first anneal step is negligible.

R0 of the 15/200 nm Ta/Pt sample, annealed at 1000 (250^1) °C is quite constant compared to the 950 °C sample.

The TCR increases slightly, therefore can be concluded for this film composition, the degradation is in conformance with the earlier described relation between R0/the TCR and the anneal temperature for 15/200 nm Ta/Pt.

For the 220 nm Pt sample, annealed at 1000 (250^1) °C, compared to the 950 °C sample, R0 and the TCR increases slightly. This is quite in conformation to the earlier described relation between R0/the TCR and the anneal temperature.

For the 15/100 nm Ta/Pt sample, annealed at 1000 (250^1) °C, R0 is like all other samples annealed above 650 °C, not clearly related to the anneal temperature. The TCR of the sample annealed at 1000 (250^1) °C is lower than the TCR of the sample annealed at 950 °C. This is the opposite compared to the two other layer structures. It can be concluded for the 15/100 nm Ta/Pt sample annealed at 1000 (250^1) °C, it's too heavily degraded to find a relation between R0/the TCR and the anneal temperature.

5.2 Physical analysis

Several physical properties of the sample are investigated. The adhesion of the thin platinum film is tested, height profiles are measured and pictures using the microscope are made for visual inspection of the samples. The results of these measurements are discussed subsequently in § 5.2.1-5.2.3

5.2.1 Adhesion test

15/100 nm Ta/Pt, 15/200 nm Ta/Pt and 220 nm Pt

The results of the adhesion test of all samples after every anneal step is that all samples past the test. This means also all samples with platinum without adhesion layer past the test. This is quite surprisingly and indicates this procedure of depositing Pt without an adhesion layer worked out very well.

5.2.2.1 Heights: basic results

15/100 nm Ta/Pt, 15/200 nm Ta/Pt and 220 nm Pt

Height profiles of all samples are determined using the Dektak. The determined heights are the analytical average of the height profiles and are displayed in figure 12.

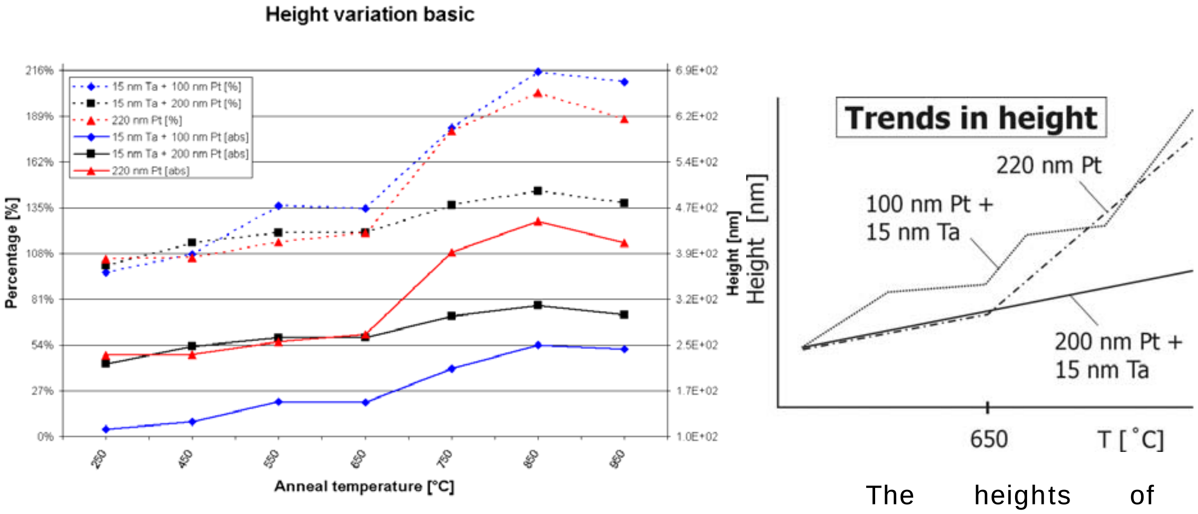

Figure 12 Height as a function of the anneal temperature (ramp up speed 10 °C/min, hold time 1 hour, passive cool down) for several layer compositions. Right hand side: trends in height.

The heights of samples of 15/200 nm Ta/Pt are roughly a linear function of the anneal temperature. This indicates degradation increases at higher anneal temperatures.

No clear relation can be found between the height of samples of 15/100 nm Ta/Pt and the anneal temperature. For anneal temperatures above 650 °C a strong increase of the height can be observed. This indicates a strong degradation of the thin platinum film for these anneal temperatures.

The heights of samples of 220 nm Pt are a linear function of the anneal temperature, up to including 650 °C. For higher anneal temperatures a strong increase is observed. This indicates strong degradation for anneal temperatures of 650 °C and higher. This is illustrated in figure 11.

5.2.2.2 Heights: other results

15/100 nm Ta/Pt, 15/200 nm Ta/Pt and 220 nm Pt

The results of the other measurements are summarized in figure 13 and discussed in § 5.2.2.2.1-5.2.2.2.2

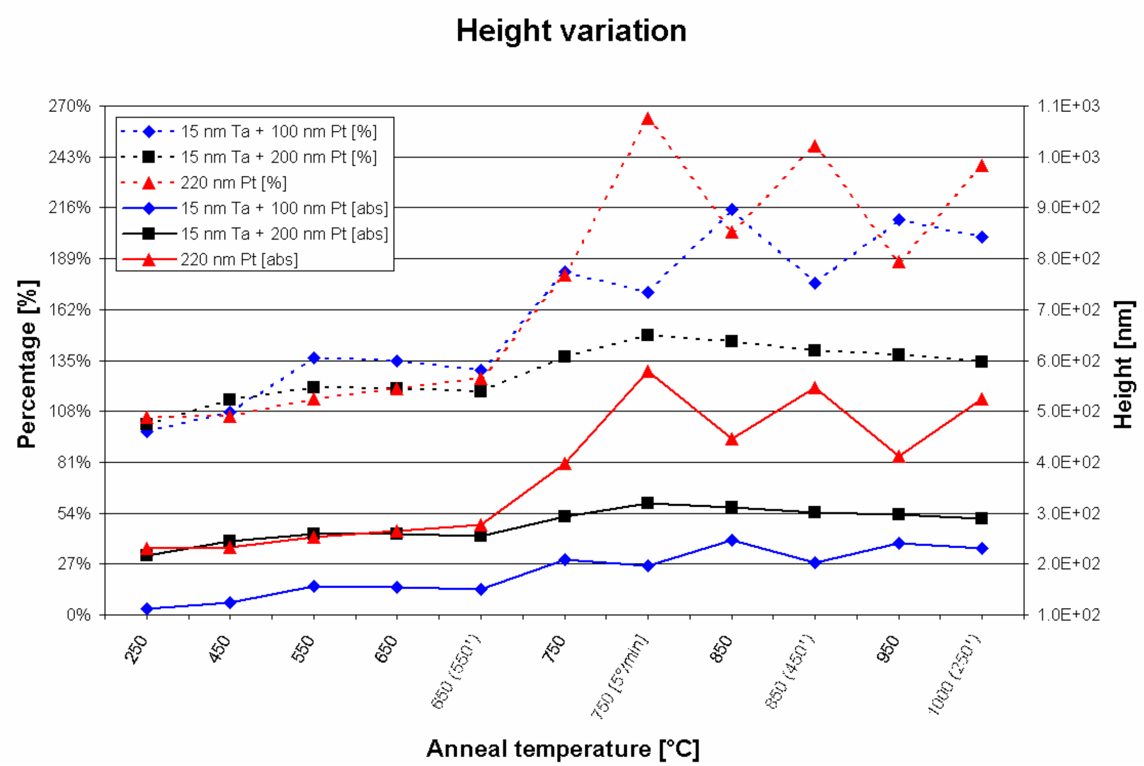

Figure 13 Heights of structures as a function of the anneal temperature for all samples and for several layer compositions.

5.2.2.2.1 Heights annealing with different ramp up speeds

15/100 nm Ta/Pt, 15/200 nm Ta/Pt and 220 nm Pt

Analogue to the electrical analysis in § 5.1.2.4, samples are annealed at the same anneal temperature with two different ramp up speeds.

The heights of samples with 15/200 nm Ta/Pt and samples with 220 nm Pt annealed at 750 °C with 5 °C/min are higher than samples annealed at 750 °C with 10 °C/min. Difference between the 220 nm Pt film samples is much more dramatic.

However, the height of the sample of 15/100 nm Ta/Pt annealed at 750 °C with 5 °C/min is (much) lower than the sample annealed with 10 °C/min. This is striking because this indicates a decrease of degradation of the sample annealed with 5 °C/min, while between the two types of samples an increase of the degradation can be observed.

5.2.2.2.2 ***Heights for annealing at two different temperatures for one sample (2-step)***

15/100 nm Ta/Pt, 15/200 nm Ta/Pt and 220 nm Pt

Similar to the electrical properties, also the heights were measured after the second anneal run.

Heights of samples annealed at 650 (550^1) °C of 100 nm and 200 nm Pt on Ta are slightly lower compared to heights of samples annealed at 650 °C. This indicates less severe degradation of thin Pt/Ta layers annealed in two steps, compared to one step annealed samples. The height of the 220 nm Pt film annealed at 650 (550^1) °C is higher than the height of the sample annealed at 650 °C. This indicates a stronger degradation of the two step annealed sample.

Heights of samples annealed at 850 (450^1) °C of 100 nm and 200 nm Pt on Ta are lower compared to heights of samples annealed at 850 °C. The difference of the 15/100 nm Ta/Pt is much larger compared to the difference of the 15/200 nm Ta/Pt sample. This indicates also less severe degradation of thin Pt/Ta layers annealed in two steps, compared to one step annealed samples. Also this indicates that the 15/100 nm Ta/Pt samples are much more be susceptible to the difference between one step and two step anneal treatments. In contrast, the height of the 220 nm Pt film annealed at 850 (450^1) °C is much higher than the height of the sample annealed at 850 °C. This indicates a stronger degradation of the two step annealed sample.

Heights of samples annealed at 1000 (250^1) °C of 100 nm and 200 nm Pt on Ta are lower compared to heights of samples annealed at 950 °C. The difference of the 15/100 nm Ta/Pt is a little bigger compared to the difference of the 15/200 nm Ta/Pt sample. This indicates also less severe degradation of thin Pt/Ta layers annealed in two steps, compared to one step annealed samples and again confirmes the 15/100 nm Ta/Pt samples is more be susceptible to the difference between one step and two step anneal treatments.

the height of the 220 nm Pt film annealed at 1000 (250^1) °C is much higher than the height of the sample annealed at 950 °C. This indicates a stronger degradation of the two step annealed sample.

5.2.3 Visual inspection

From most samples pictures are made using a microscope. To chart and compare degraded samples by visual inspection, different degradation phenomena are distinguished and separately evaluated on scale from [0..10]. Also the earlier discussed height increase measured using the Dektak are taken into account. The terminology of the effects is explained in figure 15.

5.2.3.1 15/100 nm Ta/Pt

Table 4 Inventory of different degradation phenomena for samples of 15/100 nm Ta/Pt.

15/100 nm Ta/Pt Anneal temperature [°C]	650	650 (550^1)	750	750 [5/min]	850	850 (450^1)	950	1000 (250^1)
Hillocks/Crystals [0-10]	3	3	5	6	1	2	0	0
Terracing [0-10]	0	0	0	3	8	8	0	0
Holes/Segragation/Islands [0-10]	0	0	0	0	8	7	10	10
Edge effect [0-10]	0	0	3	6	9	10	3	3
Height profile change [%]	135%	130%	182%	171%	215%	176%	209%	200%
Roughness profile [0-10]	2	2	2	3	3	3	4	4

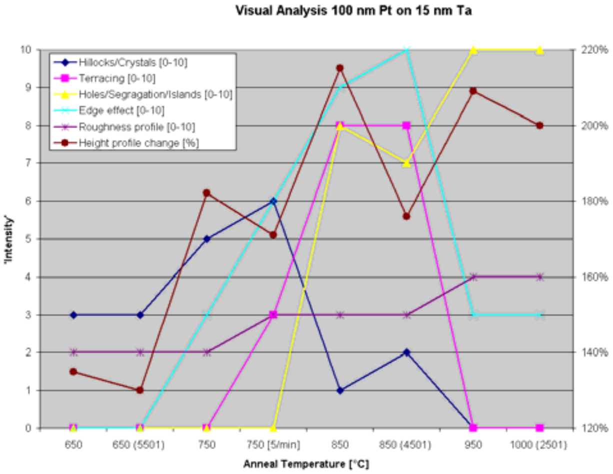

Figure 14 Plots Table 4 for 100 nm Pt on 15 nm Ta.

When looking at the results of the visual inspection of samples of 15/100 nm Ta/Pt, displayed in table 4 and figure 14, a trend can be noticed.

For anneal temperatures up to including 750 °C, the number of crystals or hillocks increases. For anneal temperatures of 850 °C, the number of hillocks decreases and the intensity of 'terracing' strongly increases. For anneal temperatures of 950 °C and above, the number of hillocks/crystals and also the intensity of the terracing further decrease. For these temperatures the number of holes and isolated islets increases.

This indicates a degradation process in which for increasing anneal temperatures up to including 750 °C first the formation of hillocks or crystals, for temperatures of 850 °C and above the flattening of those crystals resulting in the roughened terracing situation. Simultaneously in this rough film holes occur and finally the perforated film fragments into separate islets of platinum. This process is illustrated in figure 15.

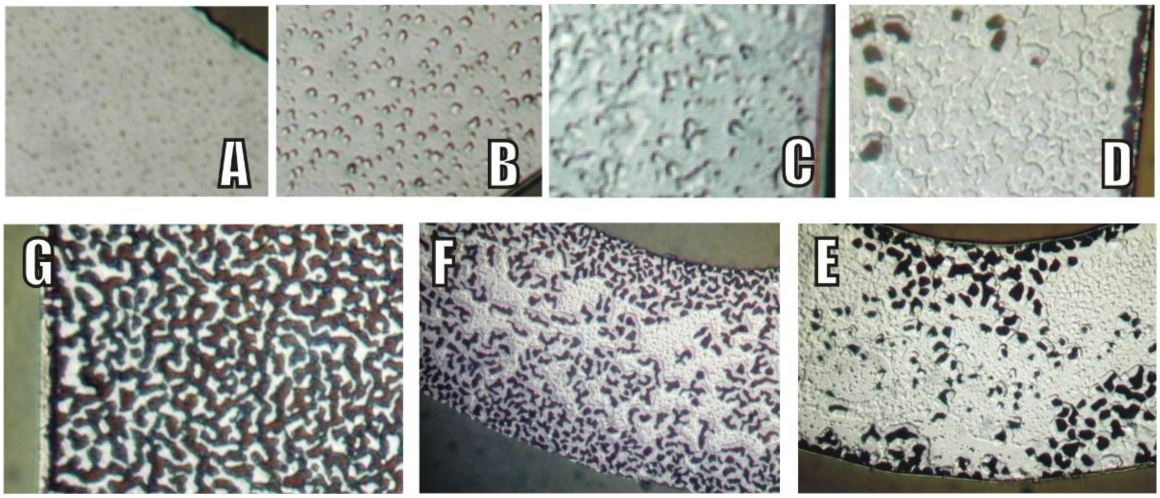

Figure 15 The visual degradation process of 15/100 nm Ta/Pt (clockwise): A:(650℃,1000x) light crystallisation of the platinum surface, B: (650℃, 1000x) stronger crystallisation of the platinum surface, C: (750℃, 1000x) flattening of the crystals resulting in the terracing situation, D: (750℃, 1000x) stronger terracing and the formation of holes, E: (850℃,200x) increasing number of holes, F: (850℃, 200x) formation of segregated islets locally, G: (1000℃, 1000x) the final deformation of the complete platinum film in a collection of separate islets of platinum.

An overall increase of the height of the film is noticed, which is in accordance with this theory. From the slight increase of the roughness of the film can be concluded that the surface of the terrace and the finally degraded situation are quite smooth.

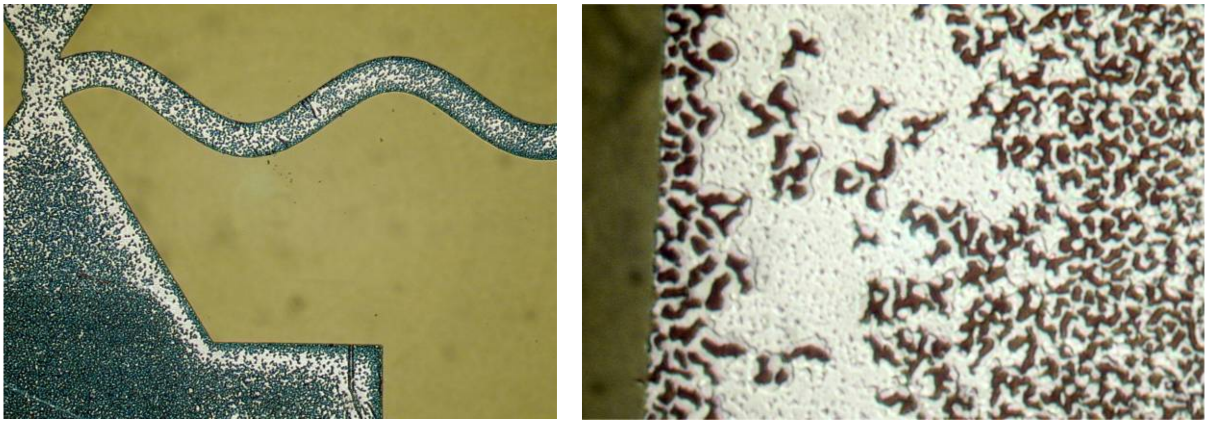

Figure 16 The edge effect: a 100 nm Pt on 15 nm Ta sample annealed at 850℃,

Left: overview (200x), right: close up at the rim (1000x)

A striking phenomenon that is noticed by the examination of the pictures is that the degradation is worse on the edge and in the centre of the platinum film. A ring between the edge and the centre is less degraded. This is referred to as the 'edge effect' and is for temperatures of 750 °C and above clearly noticeable. This is illustrated in the characteristic pictures in figure 16.

When comparing the results of the visual inspection of the sample annealed at 650 (550[1]) °C to the samples annealed in one step on the same temperature, the same degradation level can be noticed. Only a small difference in the height of the film can be noticed. For the sample annealed at 850 (450[1]) °C compared to the sample annealed at the same temperature in one step, a small decrease of the degradation is noticed for the sample annealed in two steps. For the sample annealed at 1000 (250[1]) °C compared to the sample annealed at 950 °C no difference is noticed, because both samples achieved the maximum level of degradation. When comparing the sample annealed at 750 °C at 5 °C/min to the sample annealed at 750 at 10 °C/min, a slight increase of the degradation level is noticed.

5.2.3.2 15/100 nm Ta/Pt

Table 5 Inventory of different degradation phenomena for samples of 15/200 nm Ta/Pt.

15/200 nm Ta/Pt Anneal temperature [°C]	650	650 (550[1])	750	750 [5/min]	850	850 (450[1])	950	1000 (250[1])
Hillocks/Crystals [0-10]	3	3	5	1	6	4	5	3
Terracing [0-10]	0	0	0	6	6	6	7	7
Holes/Segragation/Islands [0-10]	0	0	0	0	0	2	7	6
Edge effect [0-10]	0	0	3	0	3	4	8	10
Height profile change [%]	120%	118%	136%	148%	145%	140%	138%	134%
Roughness profile [0-10]	1	3	1	2	2	2	1	1

The results of the visual inspection of the 15/200 nm Ta/Pt are displayed in table 5 and figure 17 and are comparable at some points to the 15/100 nm Ta/Pt sample, but at other points they differ.

For anneal temperatures of 650 °C and 750 °C , the number of crystals or hillocks increases. For the anneal temperature of 850°C, the number of hillocks still increases and the intensity of terracing strongly increases. For anneal temperatures of 950 °C and above, the number of crystals decreases while the intensity of the terracing further increases. For these temperatures the number of holes and isolated islets increase.

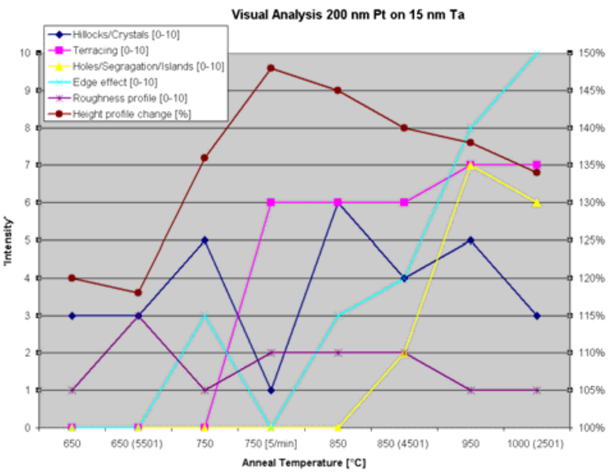

Figure 17 Plots Table 5 200 nm Pt on 15 nm Ta

This indicates to a degradation process for increasing anneal temperatures of first the formation of hillocks or crystals, for temperatures of 750 °C and above the flattening of those crystals resulting in the roughened terracing situation. In this rough terraced film with crystals holes occur for higher anneal temperatures (950 °C and above) and finally partly the fragmentation of the terraced perforated film into separate islets of platinum.

The terracing in the final phase of 15/200 nm Ta/Pt is much more intense compared to 15/100 nm Ta/Pt films. The islet formation is much less for the highest anneal temperatures, indicating the 15/200 nm Ta/Pt samples are not as far degraded as the equivalent 15/100 nm Ta/Pt samples. This is supported by the lesser percentage height increase the 15/200 nm Ta/Pt sample (±135% [200/15] vs 205% [100/15nm]) and the lower roughness of the film. Striking is the greater edge effect of the 15/200 nm Ta/Pt samples for high anneal temperatures.

When comparing the results of the visual inspection of the sample annealed at 650 (550^1) °C to the samples annealed in one step on the same temperature, the same degradation level can be noticed with a higher level of roughness. This is strange and probably due to a measurement of a local defect. For the sample annealed at 850 (450^1) °C compared to the sample annealed at the same temperature in one step, an increase of the degradation level is noticed for the sample annealed in two steps. For the sample annealed at 1000 (250^1) °C compared to the sample annealed at 950 °C a slight decrease of the degradation level can be noticed. This however is contradictory to the percentage height increase.

When comparing the sample annealed at 750 °C at 5 °C/min to the sample annealed at 750 at 10 °C/min, a strong increase of the terracing effect is noticed. Together with the increase of the percentage height, it can be concluded the sample annealed with 5 °C/min has a higher degradation level, compared to the sample annealed with 10 °C/min.

In summary, it can be concluded that the physical degradation level for a certain anneal temperature is worse for a 15/100 nm Ta/Pt film in comparison to a 15/200 nm Ta/Pt film, but the degradation process itself looks the same. The results for samples annealed in two steps are too different to draw conclusions from. Samples annealed at 5 °C/min have a higher level of degradation compared to equivalent samples annealed at 10 °C/min.

5.2.3.3 220 nm Pt

Table 6 Inventory of different degradation phenomena for samples of 220 nm Pt

220 nm Pt Anneal temperature [°C]	650	650 (550^1)	750	750 [5/min]	850	850 (450^1)	950	1000 (250^1)
Hillocks/Crystals [0-10]	3	4	8	8	9	9	8	6
Terracing [0-10]	0	0	6	7	7	8	9	7
Holes/Segragation/Islands [0-10]	0	0	0	0	3	5	6	7..9
Edge effect [0-10]	3	3	3	3	3	0	0	0
Height profile change [%]	120%	126%	180%	263%	180%	249%	187%	238%
Roughness profile [0-10]	4	4	7	7	7	8	5	8

The results for the visual inspection of the 220 nm Pt samples are displayed in table 6 and figure 18. For anneal temperatures up to including 650 °C, the number of crystals or hillocks increases. For anneal temperatures of 750°C and 850 °C, the number of hillocks still increases and the intensity of terracing strongly increases. For anneal temperatures of 950 °C and above, the number of crystals decreases while the intensity of the terracing further increases. Furthermore, for temperatures of 850 °C and above the number of holes and isolated islets increases.

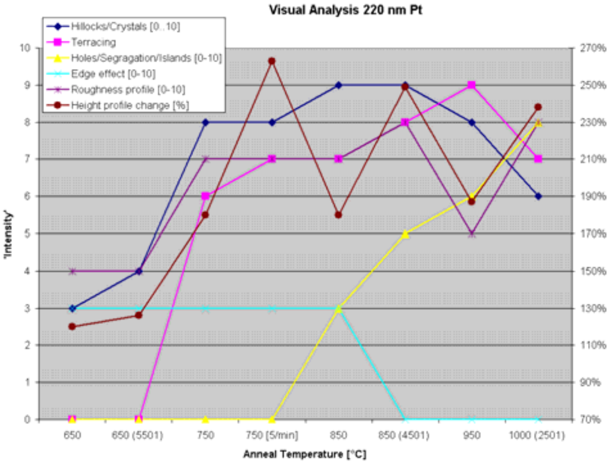

Figure 18 Plots Table 6 220 nm Pt

This indicates to a degradation process for increasing anneal temperatures of first the formation of hillocks or crystals quickly to high intensities, for temperatures of 750 °C and higher the partly flattening of those crystals resulting in the roughened terraced situation while other crystals grow even more. In this rough terraced film with big crystals, holes occur for higher anneal temperatures (850 °C and above) and finally partly the fragmentation of the terraced perforated film into pieces of platinum. The height and roughness are generally increasing for increasing annealing temperatures.

When comparing the results of the visual inspection of the sample annealed at 650 (550^1) °C to the samples annealed in one step on the same temperature, almost the same degradation level is noticed. For the sample annealed at 850 (450^1) °C compared to the sample annealed at the same temperature in one step, a dramatic increase of the degradation level is noticed for the sample annealed in two steps. For the sample annealed at 1000 (250^1) °C compared to the sample annealed at 950 °C an increase of the degradation level can be noticed. This is in accordance to the percentage height increase.

When comparing the sample annealed at 750 °C at 5 °C/min to the sample annealed at 750 at 10 °C/min, almost the same level of degradation is noticed. This is striking and in contradiction with the height analysis, because the difference in the percentage height increase is more then 80%, indicating a much higher degradation level of the sample annealed with 5°C/min.

The samples of 220 nm Pt can be compared best to the 15/200 nm Ta/Pt samples because of the Pt layer thicknesses. The crystallisation of the 220 nm Pt samples is much more intense compared to samples of 15/200 nm Ta/Pt.

The terracing in the final phase is also a little more intense compared to 15/200 nm Ta/Pt films. For annealing at 850 °C for 220 nm Pt samples holes already occur in the crystal rich film, while the 15/200 nm Ta/Pt film still dense is. The islet formation is a little worse for the highest anneal temperatures. The roughness and the percentage height increase is much higher compared to 15/200 nm Ta/Pt. This indicates the 220 nm Ta/Pt samples have a higher degradation level for a certain anneal temperature compared to 15/200 nm Ta/Pt samples. Striking is also the much lesser edge effect of the 220 nm Pt samples for anneal temperatures of 850 °C and above.

Summarizing can be concluded that the physical degradation level for a certain anneal temperature is worse for a 220 nm Pt film in comparison to a 15/200 nm Ta/Pt film. The degradation process itself looks a little different with stronger crystallisation/agglomeration and the holes start to occur at 850 °C. Furthermore the percentage height increase is much more. The results for samples annealed in two steps for high temperatures are more degraded. The two-step anneal treatment has a negative influence on the degradation level. Samples annealed at 5 °C/min have a higher level of degradation compared to equivalent samples annealed at 10 °C/min.

5.2.4 Summary physical degradation

In this paragraph all results of the physical degradation are summarized. The visual inspection is summarized in figure 19 and table 7.

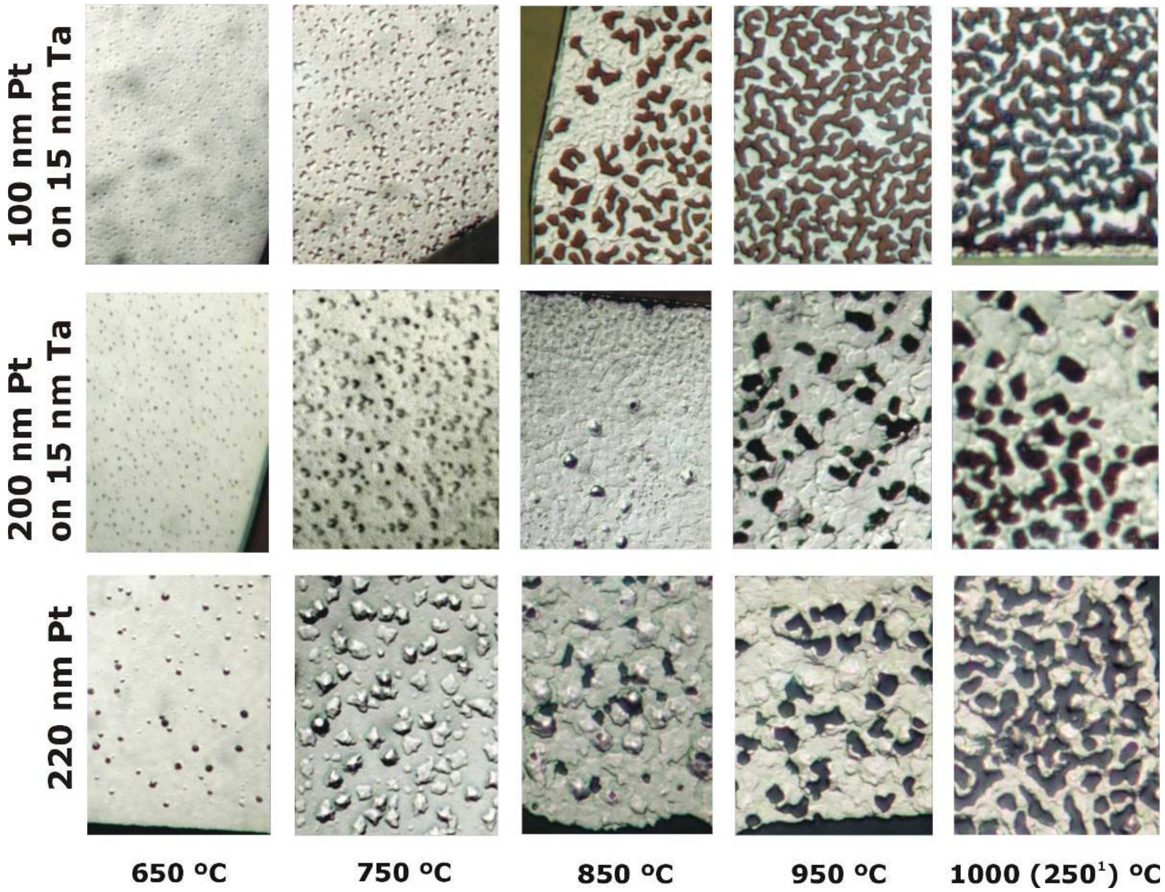

Figure 19 Typical pictures of samples of the three layer compositions, at different annealing temperatures (ramp up speed of 10 ℃/min, 1 hour hold time, passive cool down). Scale: all three layers annealed at 650 ℃ and both 15/100 nm Ta/Pt and 15/200 nm Ta/Pt annealed at 750 ℃: 500x, all other samples: 1000x)

Table 7 Summary of the visual inspection

Classification level of degradation of the different layer compositions different situations	100 nm Pt on 15 nm Ta	200 nm Pt on 15 nm Ta	220 nm Pt
Increasing anneal temperatures with ramp up speed of 10°C/min, 1 hour hold time an passive cool down	high	low	medium
Two step annealing compared to equivalent one step annealing	no difference	a bit higher	higher
Annealing with 5/min compared to equivalent samples annealed at 10/min	a bit higher	higher	no visual difference, dramatic height increase

The results of the visual inspection are summarized in table 7. 15/200 nm Ta/Pt has relatively the lowest level of degradation as a function of the standard anneal conditions, followed by 220 nm Pt. The 15/100 nm Ta/Pt have the worst relative degradation level. This is illustrated in figure 19.

The two step anneal treatment doesn't seem to have effect on the thin layer of 15/100 nm Ta/Pt and seems to have a negative effect on both thick layer structures. The influence on the 220 nm Pt samples is the worst. Annealing with a slower ramp up speed seems to have a little negative influence on the 15/100 nm Ta/Pt samples, a more negative effect on the 200 nm Pt in 15 nm Ta whereas on the 220 nm Pt sample no visual difference can be noticed. Despite no visual difference, an dramatic increase of the height is measured.

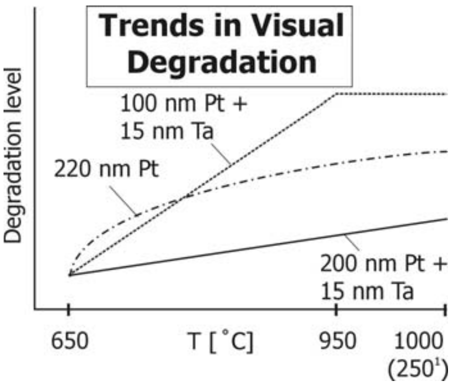

Figure 20 Trends in visual degradation

6 Conclusions

In this research project the influence of annealing of thin platinum films with adhesion layer and 'thick' platinum films with and without adhesion layer is determined. The platinum film is electrically stable (the TCR and R0 are constant) for a certain period of time when heated up to at most the anneal temperature, after annealing.

Both electrical and physical properties are considered. Trends determined in those properties are summarized in figure 16. Finally an advise is given of the best film composition to be used in the microreactor in the FORSIM project.

The temperature coefficient of resistance (TCR) is determined as a function of the anneal temperature. Annealing is done in air ambient with a ramp up speed of 10 °C/min, hold time of one hour at the anneal temperature and cooled down passively.

Experimentally is observed the that the TCR, can be determined over a temperature range of 20-60°C with an uncertainty of maximum 5 % for all layer compositions. Furthermore no hysteresis is taking place when heating up and cooling down a platinum film.

Because the R0 and TCR are better defined for high anneal temperature for both 'thick' platinum layers, these layers are preferred for use in the microreactor. On basis of the physical properties, both 'thick' platinum layers are better because of lower degradation levels, compared to the thin platinum layer. No deciding difference between layers with and without adhesion layer is determined so both layers are usable for application in the microreactor. Also the influence of annealing in two steps is studied and seems to have only a slightly positive effect on the thin platinum films, and a negative effect on both 'thick' films. Finally the influence of a slower ramp up speed of the annealing is investigated and for all three layer compositions a negative influence is determined for both electrical and physical properties.

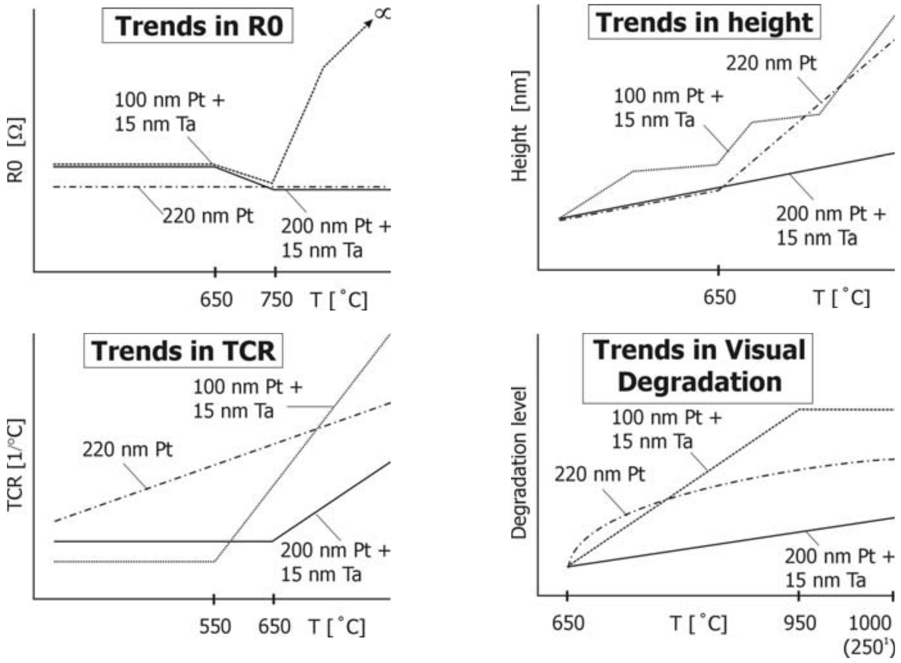

Figure 21 Summary of the trends in R0, height, TCR and visual degradation.

7 Recommendations

The main thing that has to be further investigated is the long term stability of the different layers after annealing. As mentioned in the theory, the degradation of a thin platinum film is always happening. The only difference for higher temperatures is that it occurs much faster than at lower temperatures. Actually, the 'life time' of samples annealed at certain temperatures should be determined by subjection the samples to electrical duration tests at different temperatures between room and the anneal temperatures. The time for which the electrical properties are not stable anymore ('lifetime') has to be determined. Based an these experiments, a better choice can be made between 15/200 nm Pt and 220 nm Pt.

Another thing that has to be measured in those breakdown tests is the stability of the TCR and the R0 at a certain temperature for certain amount of time. This is especially important for the application of the thin platinum film as temperature sensor: a change in the R0 and TCR during the stay at a certain temperature would result in drift in the measured temperature.

A more fundamental thing that could be investigated is the degradation process itself. What is happening to the platinum films at high temperatures , with and without adhesion layer, is still not understood fully. This is a very complex process and can be clarified by an investigation of a chemist or physicist in a PhD project.

8 References

[1] http://www.saburchill.com/physics/chapters/0037.html

[2] http://www.pilleux.cl/mt771/apuntes/05ElectronesEnMetales/Conduction.htm

[3] R.P. Reed & A.F. Clark, *Materials at low temperatures*, American Society for Metals, Ohio 1983, ISBN 0-87170-146-4

[4] http://www.allaboutcircuits.com/vol_1/chpt_12/6.html

[5] T.J. Coutts, *Electrical conduction in thin metal films*, Elsevier Scientificic Publishing Company, Amsterdam 1974, ISBN 0-444-41184-4, p 126.

[6] http://content.honeywell.com/buildings/components/Hycal_Html/temp.html

[7] http://www.materials.jhu.edu/Academics/510_605%20Electronic%20Optical%20Magnetic/Subject%2013%20Electrical%20Conductivity%20of%20Metals.pdf

[8] S.M. Firebaugh, *Investigation of Materials for Use in High-Temperature, Thin-Film Heaters and Temperature Sensors*, B.S.E., Princeton University, 1995.

[9] M.P. Moret, M.A.C. Devillers, F.D. Tichelaar, A. Aret, P.R. Hageman, P.K. Larsen, *Damage after annealing and aging at room temperature of platinized silicon substrates*, Elsevier Science, 7 feb. 2003.

[10] http://isaac.phys.um.edu.mt/NOTES/PHY3310/4-06.doc

[11] S.M. Firebaugh, K.F. Jensen & M.A. Schmidt, *Investigation of High-Temperature Degradation of Platinum Thin Films with an In Situ Resistance Measurement Apparatus*, Journal of microelectromechanical systems, Vol. 7, No 1, march 1998.

[12] K. Sreenivas, I. Reaney, T. Maeder, N. Setter, C. Jagadish & R.G. Elliman, *Investigation of Pt/Ti bilayer metallization on silicon for ferroelectric thin-film integration*, Journal of Applied Physics, 75 (1): 232-239 JAN 1 1994.

[13] Online version of the periodic table of elements/parameters elements
http://www.webelements.com/webelements/elements/text/Pt/heat.html

[14] R. Srinivasan, *Microfabricated Reactors for Partial Oxidation Reactions*, B. Tech., Indian Institute of Technology, Bombay 1992.

[15] J.P. Evans, *High temperature platinum resistance thermometry*, National Bureau of Standards Washington D.C., 1972, 899-906.

[16] C. Alépée, *Technologies for high-temperature silicon microreactors*, Institute of Microsystems, Micro-Engineering Department, EPFL, Swiss Federal Institute of Technology, Lausanne, October 2000.

[17] "R.M. Tiggelaar - *Silicon-technology based microreactors for studying high-temperature heterogeneous gas phase reactions*; PhD-thesis; MESA+ Research Institute - University of Twente, Enschede, The Netherlands, to be published (2004)"

[18] M.J. Kim, L.A. Gruenke, R.J. Saia, S.S. Cohen, *Inhibition of acid etching of Pt by pre-exposure to oxygen plasma*; Appl. Phys. Lett 33(4), 1984, pp 462-464.

[19] J. Strong - *On the cleaning of surfac*es; Rev. Sci. Instr., 6, (1935), pp. 97-99.