Platinum metallization for MEMS application

Focus on coating adhesion for biomedical applications

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The adherence of Platinum thin film on Si/SiO₂ wafer was studied using Chromium, Titanium or Alumina (Cr, Ti, Al₂O₃) as interlayer. The adhesion of Pt is a fundamental property in different areas, for example in MEMS devices, which operate at high temperature conditions, as well as in biomedical applications, where the problem of adhesion of a Pt film to the substrate is known as a major challenge in several industrial applications health and in biomedical devices, such as for example in the stents.¹⁻⁴ We investigated the properties of Chromium, Titanium, and Alumina (Cr, Ti, and Al₂O₃) used as adhesion layers of Platinum (Pt) electrode. Thin films of Chromium, Titanium and Alumina were deposited on Silicon/Silicon dioxide (Si/SiO₂) wafer by electron beam. We introduced Al₂O₃ as a new adhesion layer to test the behavior of the Pt film at higher temperature using a ceramic adhesion thin film. Electric behaviors were measured for different annealing temperatures to know the performance for Cr/Pt, Ti/Pt, and Al₂O₃/Pt metallic film in the gas sensor application. All these metal layers showed a good adhesion onto Si/SiO₂ and also good Au wire bondability at room temperature, but for higher temperature than 400 °C the thin Cr/Pt and Ti/Pt films showed poor adhesion due to the atomic inter-diffusion between Platinum and the metal adhesion layers.⁵ The proposed Al₂O₃/Pt ceramic-metal layers confirmed a better adherence for the higher temperatures tested.

Introduction

Platinum thin film layers on Si/SiO₂ wafer are nowadays receiving considerable attention for many MEMS devices which operate at high temperature conditions, as for example micro-machined chemoresistive sensors for gas detection.^{6,7} In application of MEMS devices as sensors for gas detection, for example, the high temperature working condition (from 400 °C to 700 °C) of the sensing layer is maintained using a microhotplate as heating system. Because of the Platinum poor adhesion on Si/SiO₂, an adhesion inter-layer is deposited between Si/SiO₂ and Pt. At room temperature a Chromium film can be used as adhesion inter-layer, but not in corrosive environment and higher temperature, due, respectively, to its high oxidation and inter-diffusion rate. A Titanium adhesion layer is an alternative for corrosive environment but not for higher temperatures. For higher temperature, up to 400 °C, is possible to take place an atomic inter-diffusion between Pt and the adhesion metallic layers. This inter-diffusion process changes the electric conductance properties of the Platinum bulk, increasing the electric resistance and reducing the adhesion to Si/SiO₂.

The introduction of Alumina, a ceramic adhesive thin film, used as new adhesion inter-layer, proved to be a good solution, for MEMS devices with a Pt thin film, to work at high temperatures

and in biological environment. Alumina is a ceramic electrical insulator and has a relatively high thermal conductivity appropriate for heating systems. It resists to strong acid and alkaline attack at elevated temperatures, and at higher temperature increases the advantage associated to using Alumina as adhesion interlayer. With strong ionic interatomic bonding, the Alumina can exist in several crystalline phases and all revert to the most stable hexagonal α phase at elevated temperatures (<http://www.accurat.com/alumox.html>). Due to importance of Si, Ti, Al₂O₃, Cr, and Pt as materials used in new technologies applied in biomedical processes and devices, is important to study the interaction among these materials and understand more deeply the problem of adherence, which has a fundamental role to improve the durability and safety in the application of these materials in the human body.⁸ In biomedical applications the use of silicon-based strategies is increasing despite their high cost and limited biocompatibility.⁹ Appropriate coatings are advantageous or even necessary for the acceptance and smooth functioning; in the implants in human body, for example, the surface is critical for determining the integration between the implant and the organic human environment. Titanium and its alloys are among the most common implant materials used in human body. Alumina has been used widely in various electronic, optoelectronic, sensing devices as well as in dental and orthopedic implants. Platinum

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Figure 1. MEMS fabrication process. (A) LOR 5A (Microchem Photoresist for lift off) and positive photoresist deposited by lithography on Si/SiO₂ substrate; (B) Photoresist exposure to UV light; (C) Develop resist and LOR. LOR develops isotropically, creating a bi-layer reentrant sidewall profile; (D) Deposited films. The re-entrant profile ensures discontinuous film deposition; (E) Lift-off bi-layer resist stack, leaving only the desired film.

is used to make essential components for a range of medical devices, including pacemakers, implantable defibrillators, catheters, stents, and neuromodulation devices. The properties of platinum which make it suitable for medical device applications include its biocompatibility, inertness within the body, durability, electrical conductivity, and radiopacity. More recently, its unique properties have been exploited in catheters that incorporate platinum components for the treatment of brain aneurysms. Afterwards, a small tubular device, the stent, is usually inserted in catheters in order to keep the newly-cleared artery open. The successful development and implementation of these strategies in health care are intrinsically expected to improve the clinical performances of medical devices, thus enhancing the life quality of patients, significantly lowering medical treatment costs and providing new technological solutions.⁹

Results

MEMS fabrication process

Devices for testing structure produced using silicon-based technology have been designed using L-Edit Tanner tools. The chip has been fabricated using microtechnology. The starting material for electrodes fabrication was (100) 4-inch, p-type silicon wafer, CZ double polished. The structure has been realized onto the substrate by a 500-nm-thick layer of silicon oxide growth by thermal wet oxidation followed by a 150-nm-thick stoichiometric Si₃N₄ film deposited by LPCVD (Low Pressure Chemical Vapor Deposition). A further insulating multilayer (500-nm undoped TEOS oxide) was deposited. A Cr/Pt, Ti/Pt or Al₂O₃/Pt different layers have been deposited by evaporation on the front trough a negative photoresist and etched with a lift off technique. After initial period, the stability of platinum heater fabricated in this way was satisfactory at temperature up to 450 °C (about 0.01% drift per day) (Fig. 1). The TCR value measured at T₀ = 20 °C was 2800 ppm/°C.

Sheet resistance measurements

Figure 2 shows the sheets electrical resistance testing machine obtained by a four point prober. The electrical resistance, shown in Figure 3, was repeated in three different positions on the surface of the samples, to verify the eventual fluctuation of resistance.

Figure 2. Sheet resistance measured by digital four probe station (Napson RG-8).

The standard deviation showed a very little fluctuation depending on position on the surface. The electrical resistance decreased with the increasing of annealing temperature for all samples. It's also possible to note that until 600 °C the samples in Nitrogen flow processing conditions presented a slightly lower resistance. The Alumina samples showed a behavior like Titanium samples, with lower resistance than Chromium.

Temperature coefficient of resistance (TCR)

The TCR coefficient describes the electrical resistance behavior vs. annealing temperature and it is quoted in terms of parts per million per degrees Centigrade.

The term “ppm/°C” is not specific to resistors, but applies to almost every single electronic component ever produced and is a measure of how much the component's stability will drift in response to a change in temperature. That is usually measured in terms of “parts per million per degrees centigrade” (ppm/°C). The meaning of “parts” is the unit used in the measure of that component; in this case it is Ohms.

It is important to evaluate a curve of the resistance vs temperature ($R(T)$) of the sensors in laboratory conditions to obtain their thermal behavior. For this purpose we designed a dedicated oven. The oven's chamber has a socket for the sensor and it is electrically connected through isolated wires and it is possible

Figure 3. The sheets electrical resistance.

Figure 4. TCR behavior vs. annealing temperature for samples with Alumina, Titanium or Chromium as adhesion layer, under oxygen or nitrogen gas flow.

Figure 5. SEM images of Al₂O₃/Pt film indicate a modification of the surface due to annealing at 500 °C. (A) and (B) Samples surface after a 400 °C annealing; (C) and (E) 700 °C annealing with Oxygen flow, with appearing of black points; (D) and (F) 700 °C annealing with Nitrogen flow.

Table 1. Summary of the annealing treatment.

Layer	Thickness (nm)	Heating rate °C/min	Flux (sccm)		Lithography	Temperature range (°C)
			O ₂	N ₂		
Al ₂ O ₃ /Pt	5/150	10	32	32	positive	300 to 700
Cr/Pt	5/150	10	32	32	positive	300 to 700
Ti/Pt	10/150	10	32	32	positive	300 to 700

to measure three different resistances at the same time, controlling the heating rate and recording every data in the computer. Elaborating these data are possible to know the equation of the curve and the Temperature Coefficient Resistance (TCR) of the sensor.

Figure 4 shows the TCR values of the samples depending from annealing temperatures and from gas flow. In this work was realized a preliminary study of the TCR behavior of the samples, to indicate how the resistance is changing with growing of temperature in different atmosphere conditions. So the measure was realized one single time for every condition of temperature and gas. In all samples the TCR coefficient increased with increasing of annealing temperature; this behavior was more efficient using an oxygen gas flow than a nitrogen gas flow. The Titanium and Alumina samples had a similar behavior.

Image analysis: SEM characterization

Through SEM images, showed in the Figure 5, is possible to verify the surface aspect after annealing for Alumina samples. Until 500 °C, the surfaces for all samples haven't alterations, for 600 °C and 700 °C in the corners of the Platinum surfaces are present similar alterations. For samples with Oxygen flow the

surfaces present black points. Although these modifications, the adhesion of Al₂O₃/Pt film and the electrical properties continued stable.

Image analysis: FEG characterization

Through FEG analysis, showed in the Figure 6, is possible to verify the surface aspect and to compare the presence of defects on different samples, depending from the annealing temperature and from the adhesion interlayer.

The picture of FEG characterization of the sample with Cr adhesion interlayer show the presence of defects in the surface, that seem like holes, when the annealing was carried out at 700 °C (Fig. 7D). That was probably due to tension between the surface of Si and the deposited film of Cr, more effective in the higher temperature.

The FEG image of sample with Al₂O₃ interlayer, annealed at 700 °C, showed the presence of very little defect at the surface, when compared with the defect of samples with Cr interlayer annealed at the same temperature; the presence of that little defects didn't affect the electrical properties of that samples.

The FEG images of surface of the samples with Ti interlayer didn't show any difference depending from annealing

Figure 6. FEG images, with magnification of 10.000 X. The pictures show the surface of samples with Al₂O₃, Cr, and Ti adhesion layer, annealed to 300 °C and 700 °C in a Oxygen flow. (A) and (B): Al₂O₃ interlayer, with annealing of 300 °C and 700 °C. (C) and (D): Cr interlayer, annealed at 300 °C and 700 °C. (E) and (F): Ti interlayer, where annealing was performed at 300 °C and 700 °C.

temperature, evidencing that the surface was very stable in this range of temperature.

Discussion

We can see, through **Figure 1** and **Figure 2**, the lower yield for Chromium samples vs. Titanium and Alumina. The Chromium is a material with high inter-diffusion rate on Platinum, consequently, the adhesion force in these samples has a several reduction when annealing temperature increases. Another problem for the high inter-diffusion rate is the difficult to reach a stable

state; in others words, the electrical properties for Chromium samples change every time that we subject the sample to the same annealing temperature. The Titanium samples has a good electrical behavior for the annealing process, however the adhesion of the film can be severally reduced with the growing of annealing temperature. In all the samples the adherence of the Pt film on the surface, reached through the presence of an interlayer of Cr, Ti or Alumina, was influenced on the gas atmosphere used to anneal the samples and in higher temperatures an oxygen flow reduced the problem of a lost in adherence of the samples surface. In the evaporation of Alumina, the electron-beam evaporator produces a non-stoichiometric film due to oxygen deficiency.¹

Figure 9. Curve and photo of an annealing process in the minibrute furnace by Nitrogen gas flow.

The electrical resistance, before and after annealing, was measured by a sheet resistance test using a ST3–1 digital four point probe (Napson RG-8) at 20 °C. The Temperature Coefficient of Resistance (TCR) was calculated by measuring the change in the electrical resistance per degree of temperature, controlling the temperature using a special furnace. The TCR values were determined through the equation:

$$R(T) = R_{ref} \times [1 + \alpha(T - T_{ref})]$$

where $R(T)$ is the conductor resistance at temperature “ T ,” R_{ref} is the conductor resistance at reference temperature $T_{ref} = 0\text{ °C}$ and α is the thermal coefficient of resistance, specified for any conductor material. T and T_{ref} are, respectively, the conductor temperature and the reference temperature in degrees Celsius.

Roughness and thickness analysis were made by optical profilometry scanning (KLA – Tencor P – 15 stylus profilometer). The films adherence and the atomic interdiffusion between substrate and interlayer and between interlayer and film were studied through Optical Microscopy (Leitz Ergolux), Scanning Electron Microscopy (JOEL JSM – 6100), and through FEG-SEM

Field Emission Gun Scanning Microscopy (JEOL, SEM-FEG JSM-6701F).

Conclusions

The application of Alumina, produced by electron bombardment, as a new adhesion layer material for gas and biological sensors and in biomedical applications, appears as an excellent alternative to improve the adherence of the platinum surface on the Si/SiO₂ substrate. Alumina is electrically insulating, optically transparent, chemically stable, bio-inert and biocompatible material, with a good adhesion on Si/SiO₂ in higher temperatures and with remarkable electrical properties when used as an adhesion layer film between Si/SiO₂ and Platinum.

Disclosure of Potential Conflicts of Interest

No potential conflicts of interest were disclosed.

References

- Lewis F., Turgeon S., Chevallier P., Pireaux J.-J., Tatoulian M., Mantovani D. On the growth of fluorocarbon thin films deposited on plasma etched 316L stainless steel. *Plasma Processes and Polymers* 2009; 7: 309-317; <http://dx.doi.org/10.1002/ppap.200900107>
- Nelea V., Holvoet S., Turgeon S., Mantovani D. Deposition of fluorocarbon thin films on outer and inner surfaces of stainless steel mini-tubes by pulsed plasma polymerization for stents. *J Phys D: Appl Phys* 2009; 42: 225208; <http://dx.doi.org/10.1088/0022-3727/42/22/225208>
- Lewis F., Mantovani D. Methods to Investigate the Adhesion of Soft Nano-Coatings on Metal Substrates—Application to Polymer-Coated Stents. *Macromol Mater Eng* 2009; 249:11-9; <http://dx.doi.org/10.1002/mame.200800229>
- Lewis F., Mantovani D. Coated Stents: How to investigate the adhesion of the coating? A comparative review. *Macromol Mater Eng* 2009; 294:11-9; <http://dx.doi.org/10.1002/mame.200800229>
- Vincenzi D., Butturi MA., Guidi V., Carotta MC., Martinelli G., Guarnieri V., Brida S., Margesin B., Giacomozzi F., Zen M, et al. Development of a low-power thick-film gas sensor deposited by screen-printing technique onto a micromachined hotplate. *Sens Actuators B Chem* 2001; 77:95-9; [http://dx.doi.org/10.1016/S0925-4005\(01\)00679-7](http://dx.doi.org/10.1016/S0925-4005(01)00679-7)
- Adami A., Lorenzelli L., Guarnieri V., Francioso L., Forleo A., Agnusdei G., Taurino AM, Zen M, Siciliano P. A WO₃-based gas sensor array with linear temperature gradient for wine quality monitoring. *Sens Actuators B Chem* 2006; 117:115-22; <http://dx.doi.org/10.1016/j.snb.2005.11.006>
- Maily F., Giani A., Bonnot R., Temple-Boyer P., Pascal-Delannoy F., Foucaran A., Boyer A. Anemometer with hot platinum thin film. *Sens Actuators A Phys* 2001; 94:32-8; [http://dx.doi.org/10.1016/S0924-4247\(01\)00668-9](http://dx.doi.org/10.1016/S0924-4247(01)00668-9)
- Cowley A., Woodward B. A Healthy Future: Platinum in Medical Applications. *Platin Met Rev* 2011; 55:98-107; <http://dx.doi.org/10.1595/147106711X566816>
- Nguyen, NT. Fabrication Issues of Biomedical Micro Devices. *BioMEMS and Biomedical Nanotechnology* 2007; 2007:93–115