THIN FILMS CHARACTERISATION FOR HIGH TEMPERATURE APPLICATIONS[1]

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ABSTRACT

It is know well established that thin films can be produced by a wide variety of methods, either physical or chemical (PVD, CVD, sputtering, etc.), but in most of applications these films are produced to operate in very narrow ranges of temperatures, and its components are not subjected to differential thermal expansions, recrystalisations and grain size modifications that are present in high temperature work.

This paper reports the production and characterisation of thin films of platinum and titanium in ceramic substrates by one of the physical vapour deposition techniques, the e-gun evaporation, to be used as temperature sensors, including the choice of the materials, the determination of their thickness, density, electrical resistivity, surface roughness, and structural characterisation (X-ray, SEM, and AES). Special emphasis is given to the thermal and electrical behaviour of these films between room temperature and 1000 °C.

KEY WORDS: alumina, density, high temperature, platinum, PVD resistance, thermal sensor, thin films.

1. INTRODUCTION

Vacuum deposition of a metal film was first reported by Faraday in 1857 using exploding wires [1]. Nahrwold was the first to use thermal evaporation in vacuum to produce a thin film, in 1887. The electron beam evaporation technique has developed since 1972 to a mature technology, offering now a vast range of applications. The advantages of vacuum evaporation is that films of a variety of materials can be deposited at high rates over large areas in a very pure form.

The use of thin films for the construction of temperature sensors has received some interest, because of a few obvious advantages like the lower consumption of precious materials (i.e. platinum) and the high productivity of the already existing technology (mainly used in the semiconductor industry), making possible to obtain custom sensors, tailored for specific applications. There are also some drawbacks, such as the impossibility of reducing the size below a certain limit imposed by the actual technology and a poor intrinsic temporal stability of some thin films. This last constraint is by far the most import and is due mainly to the presence of intimate contact between two materials with rather different properties (the substrate and the film itself) as well as to some temporal and temperature evaluative processes in thin films. An example of a temporal evaluative process is the natural tendency of the atoms to rearrange themselves in the lowest energy positions on the surface of the substrate [2].

However, in addition to the desirable good adhesion properties between substrates and thin films, for high temperature conditions, the differences between the coefficients of thermal expansion of the substrate and film material can produce thermal (shrinkage) stresses that put the film in tension or in compression, depending on which material has the greater thermal

expansion. Film stresses can also change with film thickness. These stresses modify some of the properties of the films with respect to the pure metal properties.

The understanding of the metal/ceramic interfaces and the knowledge of their behaviour at high temperature plays a very important role in various aspects of electronic industries including microelectronics packaging, thin films devices and the joining of structural ceramics with metals [3]. It is assumed that the most important phenomena took place in the bulk itself and not in the surface, since the surface contribution is negligible. That assumption is no longer valid in thin films as the surface contribution in this case is far from being negligible.

The thermal sensors developed in this work are of the thin film type, consisting of a substrate and some thin film layers deposited on it. Figure 1 shows a schematic drawing of the sensor. The thickness of the film is an order of magnitude lower than the other two dimensions.

The properties of atomically deposited films depend strongly on the material being deposited, on the substrate surface chemistry and morphology, on the surface preparation process, on the details of the deposition process and the deposition parameters. Consequently, the structure of thin films is very different from the ideal crystalline lattice of the corresponding bulk material. The origin of the unique properties of physical vapour deposition (PVD) film can be attributed to the film formation process. The next sections describe in detail some of the problems previously encountered in the manufacture of metal thin films to work at temperatures near room temperature, and its possible influence in its applications at high temperatures.

1.1 Influence of the geometrical design of the thermal sensors

Regardless of the materials and the control degree of film resistance, a given geometrical pattern must be designed. The pattern is normally used to achieve the desired final sensor resistance. The methods for producing a certain pattern fall into the two following categories: selective deposition through adequate masks, the mask permitting the film material to be deposited only on the desired areas - photolithography and selective removal of material after the deposition (the material deposited over the entire substrate being removed from the non-desired areas) - chemical etching. This one is now widely used with some form of photoresist to delineate the pattern. The necessary degree of accuracy chemical etching is perhaps an order of magnitude lower than the values used in electronic technology.

1.2 Influence of the surface cleanness and adhesion

A special mention is necessary for the surface cleanness. A good adhesion and a good temporal stability can only be achieved with an ultimate degree of cleanness. Film adhesion is intimately connected with the film and substrate properties as well as the properties of the interfacial (interphase) materials and therefore, very sensitive to surface cleanness prior to the film deposit.

1.3 Influence of the substrate and leads connections:

The substrate plays a major role. It has been pointed out by Duckworth [4] that is more relevant to refer to a substrate-film system rather than a particular type of film. In some cases and

mostly at high temperatures, the film can interact with the substrate. The actual choice is high-quality alumina substrate because the chemical purity of the substrate is imperative for reproducible results. However is hard to say which is the best choice for substrate and no single materials meets all the requirements. This desired substrate properties are can be summarised in Table I.

The electrical leads pose additional problems. In most cases different materials are in contact and their interaction, especially at high temperatures, is very important. Metal/metal contacts are easier to be mastered and the metal contact must adhere well to the substrate and be compatible with externally bonded leads. Due to the low electrical signals involved in most sensors, the thermoelectric effects at the contact of the two different materials can influence the reproducibility of the measurements. Whenever possible the same metals for films and leads must be used. The electrical noise present in excess caused by imperfect contacts would drastically reduce the reproducibility of a measurement. Even the best sensor can be ruined by poor contacts (and encapsulation, too).

1.4 Effect of heat treatment on metallic thin films

Due to their specific conditions of preparations, thin films exhibit a large resistance associated with a large number of structural defects. The most important thing to be remembered is that these structural defects are associated with a situation far from equilibrium. On the other hand, the heat treatment may lead to an increase in resistance because of the effect of oxidation or agglomeration of metallic islands. The general conclusions of this analysis is that for lower

deposition rates, fewer defects are generated and their decay energy is smaller than for higher deposition rates. The decay of resistance with the heat treatment could also be explained in another way. After the deposition the film has vacancies well in excess of the equilibrium value. As stated before, thin films deposited at lower temperatures consist of small stable islands (the particles have low mobility and remain in their impact places). Raising the temperature, the island grow in size due to agglomeration. Consequently, a continuous film deposited at low temperature, becomes non-continuous on annealing. This agglomeration process is demonstrated by the large increase in resistance that usually occurs at very high temperatures. For a given substrate-material combination there is a direct connection between the thickness and the highest temperature achieved in of the annealing before agglomeration [2]. The behaviour of these films during the annealing process is too complicated to be described here, but as a general rule it can be said that there is a strong tendency towards grain growth and hence towards an increase in chemical and crystalline perfection with the "ageing" of the film.

1.5. Influence of the temporal stability

Temporal stability is one of the most important conditions for a good temperature detector. The film itself is not a very temporal-stable structure. Some structural changes related to the displacement of atoms into the lowest potential energy positions are always present. These displacements decrease with time. Consequently, the resistance has a sharp drop after the deposition and continues to decrease more and more slowly, reaching a minimum value. In practice it is not acceptable to wait a long time to achieve a natural process of ageing. A high

degree of stability can be is achieved by a properly chosen thermal ageing process. As an example, a typical resistance change of platinum sensors during a long prolonged exposure at high temperature after a proper ageing is smaller than 0.2% for 2000 hours at 350°C and smaller than 0.05% for 2000 hours are 600°C [2].

1.6 Influence of film density, surface area and residual film stress

The presence of porosity in the columnar structure, closed and open voids and pinholes means that the film density is lower than that of the bulk material and that the surface area exposed to the ambient is much higher than at the geometrical surface area. This low density and high surface area influence many film properties, such as hardness, deformation, chemical etching rate, resistivity, and index of refection. Tensile stress can be developed when the growth mechanism does not allow the deposition atoms to reach their lowest energy positions [5]. It has been proposed that the coalescence of lattice defects into "micro voids" causes the tensile stresses.

In the next section the experimental procedure designed to construct at high temperature thermal sensor with high quality characteristics is described.

2. EXPERIMENTAL PROCEDURE

The chemical etching of the alumina substrates was produced using a mixture (1:1:5) in volume of NH_4OH at 30 %, H_2O_2 130 Vol. and H_2O deionised in volume during 5 minutes at 30°C.

On a alumina substrate (RUBALIT 99,6% Al_2O_3 by Hoechst CeramTec), a titanium layer of 100 Å (Hexagonal prisms of Ti 99,99% by Balzers) and platinum strips (Pt disc 99,99% by Balzers) were deposited.

Further details of the masking processes and deposition of the metal film can be found in a prior work [6].

In this work, the prototype sensor was made of platinum, the vital part of the sensor consists of a thin platinum strip, with a width around 110 μm and a thickness of 1.0 and 2.6 μm [7]. The thickness of the platinum strips were determined using a Surface Texture Analysis System DEKTAK 3030 (horizontal resolution ≥ 0.25 μm; vertical resolution ≥ 0.01 μm).

The electrical leads were obtain by thermal compression of 0.135 mm platinum wire on a furnace (CARBOLITE HTC 16/8, with an EUROTHERM temperature controller, model 808P) up to 1180ºC in air, during 30 minutes.

An insulation spray coating layer of about 80 μm tick ("ZPY" product alumina based) was deposited above the platinum thin film in order to protect it from the environment.

Several tests were performed to the substrate and films deposited: electrical resistivity, resistance calibration, thermal stability, and structural, morphological and chemical characterisation (X-ray, SEM, and AES).

The resistance of the film was measured with a KEITHLEY 236 multimeter, appropriate to use the Van der Pauw method [8]. The electrical resistivity was obtained from these values and the known geometric parameters.

The resistance of the platinum strip was calibrated as a function of temperature, using a platinum resistance thermometer, 25 Ω (TINSLEY 5187A) and a SENATOR automatic resistance thermometer bridge, type 5840 D, at the Laboratory of Metrology and Testing, ICAT, Lisbon.

The density was determined applying a weighing method (balance METTLER PM1200 ±0.001 g) to the substrate films (rectangular sample 2.5 x 6.0 cm) before and after the platinum deposition (2.36 μm tick).

X-ray diffraction was used to characterise the alumina substrate and the platinum thin film deposited. Both faces of the alumina substrate were also observed using a Philips Difractometer PW 1730 equipped with a graphite monochromator for Cu K_α (40 kV, 30 mA) radiation.

The SEM photographs for the morphological characterisation were obtained in a JEOL - JSM 6301F. and the AES spectra used for the platinum thin film chemical characterisation were obtained in a VG MICROLAB 310 F, equipped with a CHA and a field type emission electron gun, with a 10 keV, 50 ns electron bean spatial resolution ≅100 nm.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Electrical resistivity and resistance

The resistivity was measured after each step of the heat treatment. The heat treatment started at 100 °C in steps of 100 °C for 1 hour, until 1400 °C. After each step the sample was allowed to cool to room temperature ant its resistance was measured. The resistivity was calculated knowing the length of the strip and its thickness. Figure 2 shows the variation of the resistivity of sensors

after each heat treatment, for two different thicknesses, $\varepsilon = 1.0$ and 2.62 μm [1], widths $w = 126$ μm and length $l = 51$ mm [2]. These results demonstrate that the resistivity of all sensors start to decrease due to the vacancy coalescence, reaching a minimum around 1000 °C and increasing up to 1400 °C due to the dislocation propagation, specially the film with a thickness of 1 μm, which increases by a factor of two starting at 900 °C and vaporises at 1300 °C. The sensor with a thickness of 2.62 μm reached a plateau between 1000 and 1200 °C and future annealing processes will be made up to this last temperature. After this treatment the sensors maintain the resistivity values, around 1.43×10^{-7} Ω.m, a value about 35 % greater than bulk platinum at room temperature, as expected [6]. However some of this deviation was caused by the decrease in thickness, responsible for about a 24 % change. If we extrapolate the values between 800 °C and 1200 °C, assuming that no further contraction of the thickness of the film occurred, we obtain a value of the resistivity of around 1.08×10^{-7} Ω.m, very close to the accepted value at 22 °C (1.042×10^{-7} Ω.m) [11]. This result suggests that the platinum film still accommodates a little after the heat treatment at 1200 °C, changing slightly its resistivity value, but within tolerable limits. These changes can be measured *in situ,* calibrating it during the experiments, as the resistance of each sensor as a function of temperature has to be known to obtain the temperature field in it, surrounded by different materials.

[1] Values measured before the heat treatment. Measurements after the heat treatments at 400 °C and 800 °C showed a variation in thickness to 2.14 and 1.99 μm, respectively.
[2] No changes in width or length were found after the heat treatments.

The stability of the resistance of the strip after the heat treatments and soldering is very good, as the values at room temperature stay about the same. The resistance at room temperature and before the heat treatment was around 190 Ω and 36 Ω after the heat treatment up to 1180 °C.

The resistance per unit length of the strip, measured after the heat treatment at 1200 °C, R_W / l_W and of the short connection R_S / l_S compare very well with each other, values not departing by more than 3 % [7]. This is a very good advantage of the PVD technique for the manufacturing of sensors and a necessary condition for accurate applications.

3.2 Calibration resistance vs. temperature

The temperature field at the surface of the metal film can be monitored by measuring the resistance change in the platinum strip as a function of time, if the temperature coefficient of resistance is determined. Figure 3 shows the calibration of one of the sensors in a wide range of temperature 298 to 1273 K. The data was correlated using eq.(1).

$$R = 32.4266 + 0.12699\,T - 2.3124 \times 10^{-5}(T - 273.15)^2 + 3.2035 \times 10^{-9}(T - 273.15)^3 \qquad (1)$$

where R is expressed in Ω and T in K, with an uncertainty of 0.006 Ω.

To identify any possible hysteresis in the calibration, data was obtained going up, down and up again in temperature. The deviation of the experimental points from eq. (1) can be found in figure 4, not amounting to more than ± 0.1 %.

Table II presents the values obtained for A,B and C as well as the common values encountered in the platinum thermometers. The value of the temperature coefficient of resistance

of the platinum strip, in this range, was found to be $\alpha = 3{,}9164\times10^{-3}\ K^{-1}$, with an uncertainty of $0.018214\times10^{-3}\ K^{-1}$, is a value between $3.908\times10^{-3}\ K^{-1}$ (recommended for Type I platinum resistance thermometers - 273 to 1123 K) and $3.9289\times10^{-3}\ K^{-1}$ (very pure and well annealed platinum - 273 to 1273 K) [9, 10]. This results supports the value of the resistivity obtained in the previous section. Knowing that this coefficient is very sensitive to platinum purity and annealing process, we think that the platinum film produced by vapour deposition is very pure and with enough thickness to have normal bulk electrical properties.

3.3 Density of the platinum thin film

The density of the platinum thin film was determined by a weighing method, after the heat treatment up to 800 °C, with an uncertainty better than 0.1 %. The value determined, 15511 kgm^{-3}, is 70 % lower than the density of bulk platinum (21500 kgm^{-3}) [11].

3.4 Structural, morphological and chemical characterisation

3.4.1 Structural

X-ray diffraction was used to characterise alumina substrates and the platinum thin film deposited. Both faces of the alumina were observed, and the parameters *a* e *c* calculated agreed with the values tabulated for α-Al_2O_3 [12] and Pt [13] to within 0.02 %. These values are shown in Table III.

3.4.2 Morphological

Figures 5 and 6 are SEM photographs obtained for alumina substrate and platinum film after production and after heat treatment up to 1200 °C. The surface of Pt is smoothed by the treatment, showing some small pinholes in the film. The grain size and texture is very similar to the original substrate after treatment. Preliminary depositions showed that a better adhesion between the platinum film and alumina was achieved using a 90-100 Å thin layer of titanium [14]. Figure 7 shows the alumina substrate after chemical etching, to increase adhesion, with the crystals well defined. Figure 8 shows the titanium layer obtained, found to adhere well, both to the alumina substrate and, after the platinum vapour deposit, to the platinum film.

3.4.3 Chemical

Spectra performed using the Auger Electron Spectroscopy proved that the platinum is more than 99.99% pure. This result can be observed in figure 9.

4. CONCLUSIONS

This paper reports the construction and characterisation of thermal sensors produced by vapour deposition techniques. The first prototypes show that the platinum deposited in the strip is highly pure, keeping the properties normally encountered for bulk material, except density, as the lattice parameters, the resistivity and the thermal coefficient of resistance; the heat treatment of the deposited film, produces after several cycles, a very stable and constant resistivity; the platinum strip is strongly adhered to the titanium layer and its to the alumina substrate.

From the properties observed the sensors developed have interesting behaviour, and being electrically insulated can be applied to measure temperature profiles or thermophysical properties of materials at high temperatures, if a good thermal contact is achieved. In a future work we will attempt to miniaturise this type of sensors for flexible electronic applications down to the dimensions where the described characteristics are maintained are under way.

This work was a necessary step imposed by our primary objective of developing a new instrument to measure thermophysical properties of molten materials at high temperatures[3] [7], by monitoring the temperature profile at the surface of the platinum thin film, as a function of time, when immersed in a melt. We hope to report about it soon.

5. ACKNOWLEDGEMENTS

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[3] Developed in collaboration with Imperial College, UK, Aristotle University, Greece and University of Amsterdam, Netherlands

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Table I: Properties required for a good substrate and their effect on the film properties

Atomically smooth surface	Film uniformity
Perfect flatness	Good mask definition
No porosity	Prevent outgassing
Mechanical strength	Prevent breakage
Matched thermal expansion	Prevent film stresses
Resistance to thermal shock	Prevent fractures
Chemical inertness	Permits contact with solvents

Table II: Values obtained for A,B and C and associated errors and for R(100°C)/R(0°C):

10^3 A /°C^{-1}	10^7 B /°C^{-2}	10^{11} C /°C^{-3}	R(100°C)/R(0°C)
3,9164	-7.1311	9.8795	
±0.018214	± 0.4257	± 2.7491	1.3846
3.90802[a]	-5.8020[a]	-	1.3850[a]

[a] Type I, Platinum resistance thermometers, 0-850°C[9].

Table III. Lattice parameters for α-Al_2O_3 and Pt. *a,c* are the lattice parameters

α-Al_2O_3	Experimental	[12]	Pt	Experimental	[13]
a	4.7582	4.758	*a*	3.9208	3.9231
c	12.9915	12.991	*c*	3.9208	3.9231

FIGURE CAPTIONS

Fig. 1. The thermal sensor. Schematic.

Fig. 2. Variation of the resistivity of the platinum strip with the heat treatments, for two strips with width 1 and 2.6 μm.

Fig. 3. Resistance calibration vs. temperature for the platinum thin film thermal sensor.

Fig. 4. Percentage deviation of the experimental measurements of the resistance of the thermal sensor platinum thin film as a function of temperature.

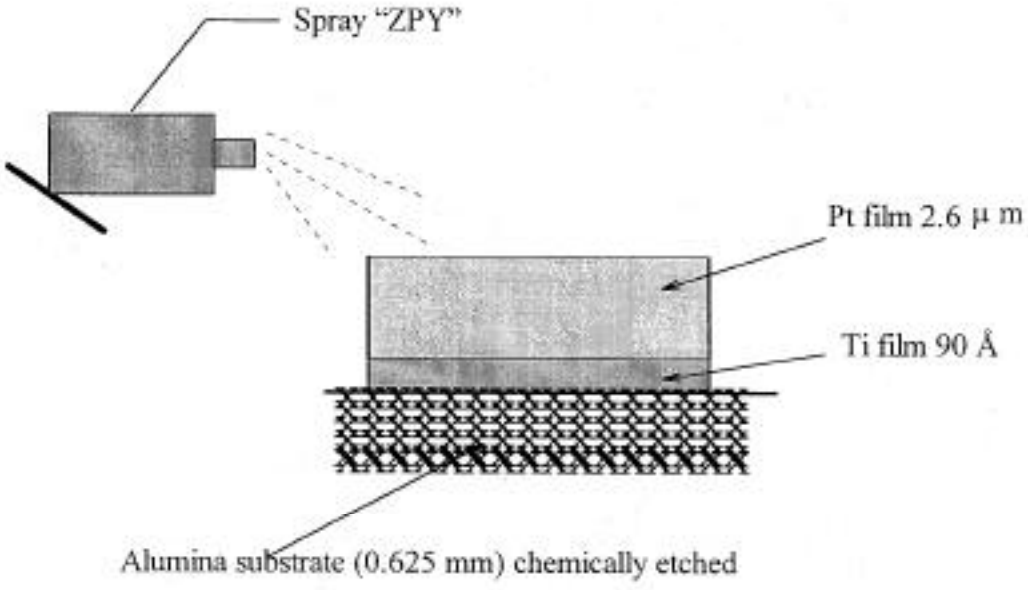
Fig. 5. SEM photograph of specific zones of the thermal sensor show the alumina (black) platinum (white) separation, before the heat treatment.

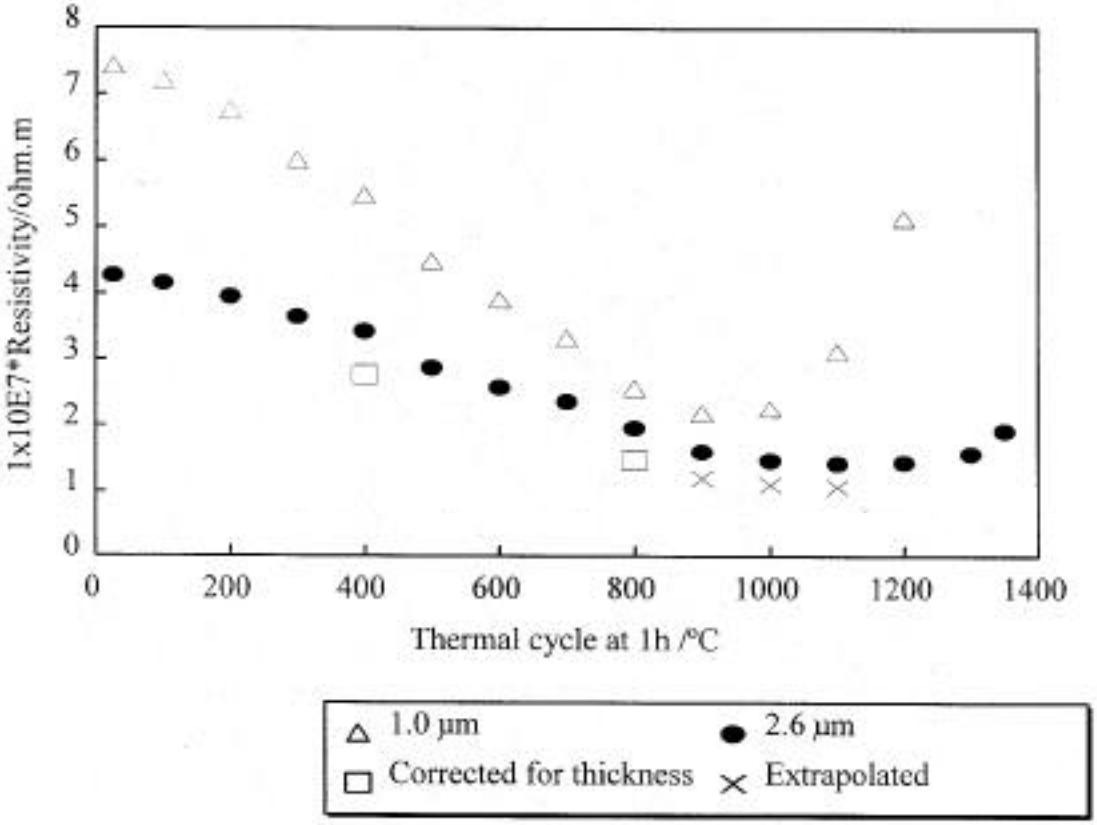
Fig. 6. SEM photograph of specific zones of the thermal sensor show the alumina (black) platinum (white) separation, after the heat treatment up to 1200°C.

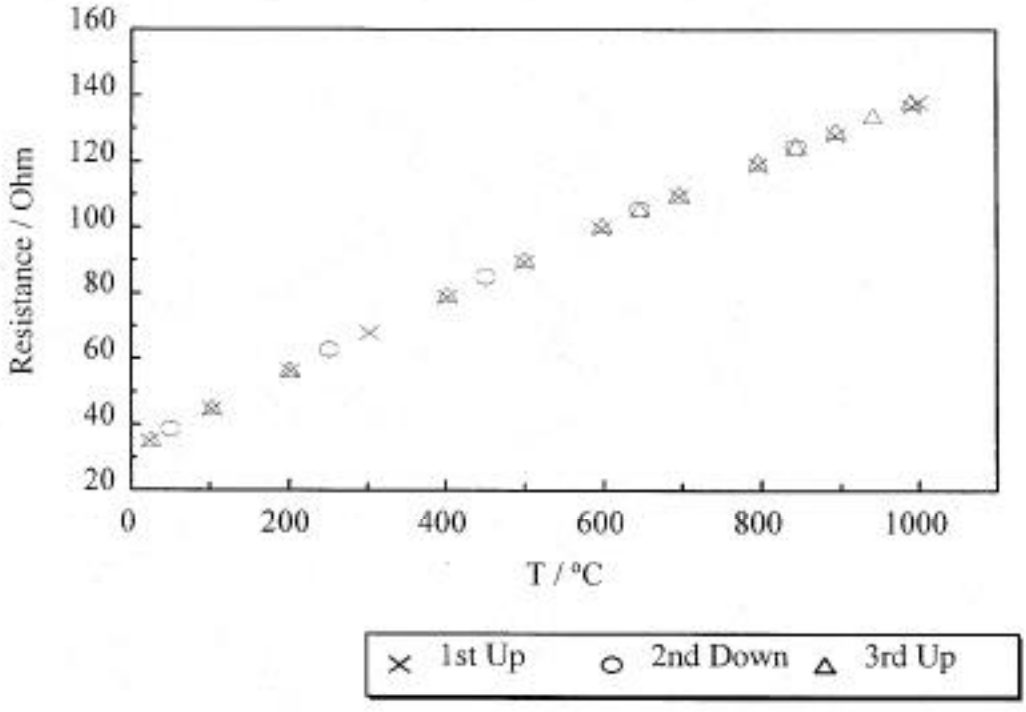
Fig. 7. SEM photograph of the thin layer of titanium (90-100 Å).

Fig. 8. SEM photograph of alumina substrate after the chemical etching.

Fig. 9. Auger spectra for platinum thin film.


Spray "ZPY"
Pt film 2.6 μ m
Ti film 90 Å
Alumina substrate (0.625 mm) chemically etched


1x10E7*Resistivity/ohm.m
0
1
2
3
4
5
6
7
8
0
200
400
600
800
1000
1200
1400
Thermal cycle at 1h /°C
1.0 µm
2.6 µm
Corrected for thickness
Extrapolated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140
120
100
80
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40
20
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400
600
800
1000
T / °C
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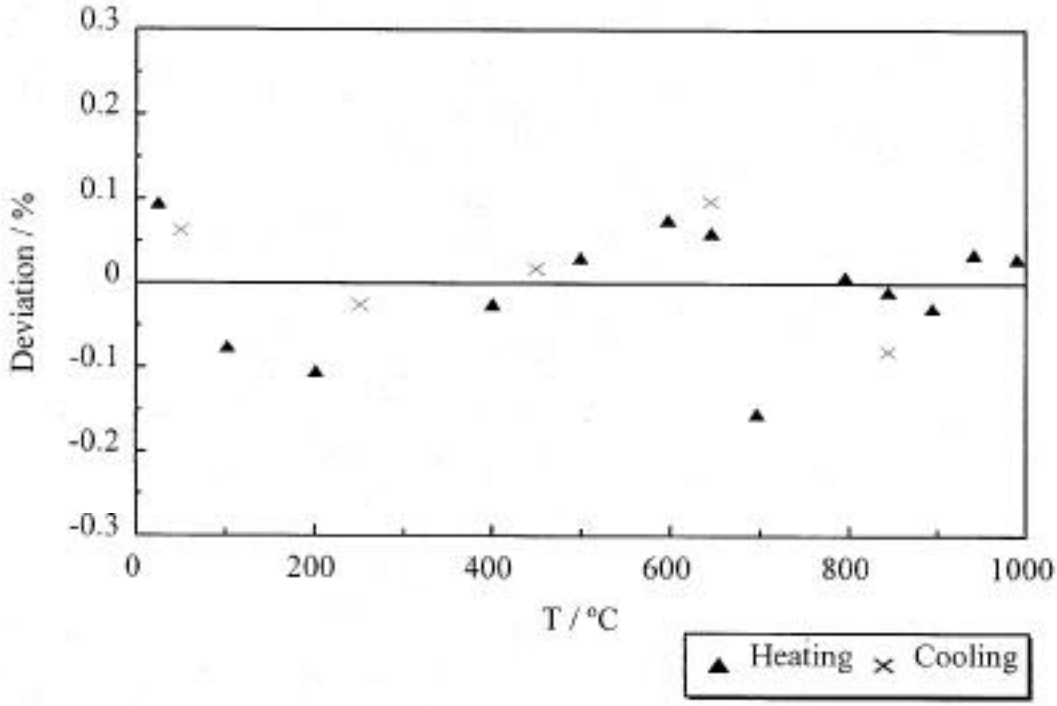
2nd Down
3rd Up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0.2
0.1
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-0.3
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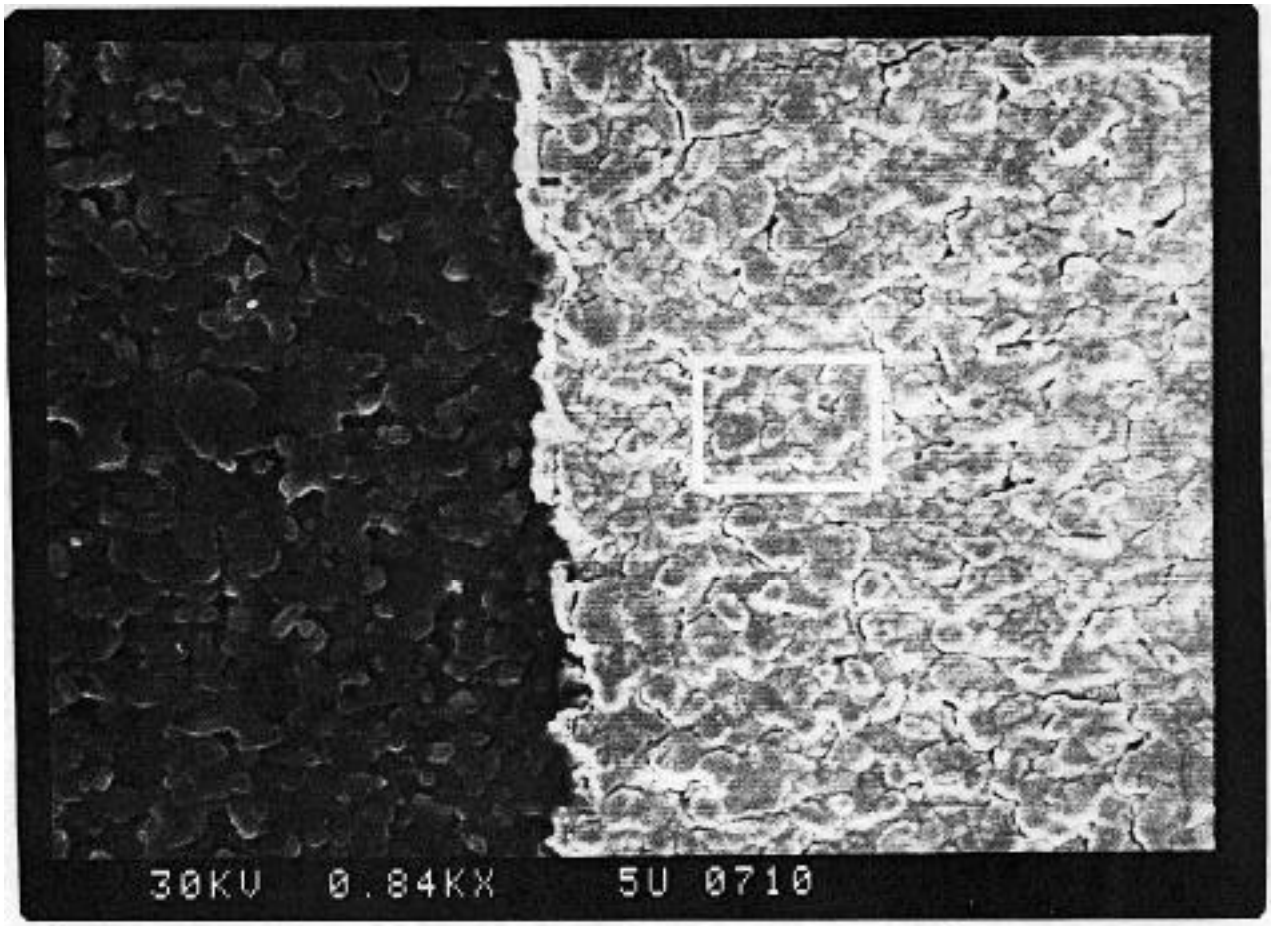
200
400
600
800
1000
T / °C
Heating
Cooling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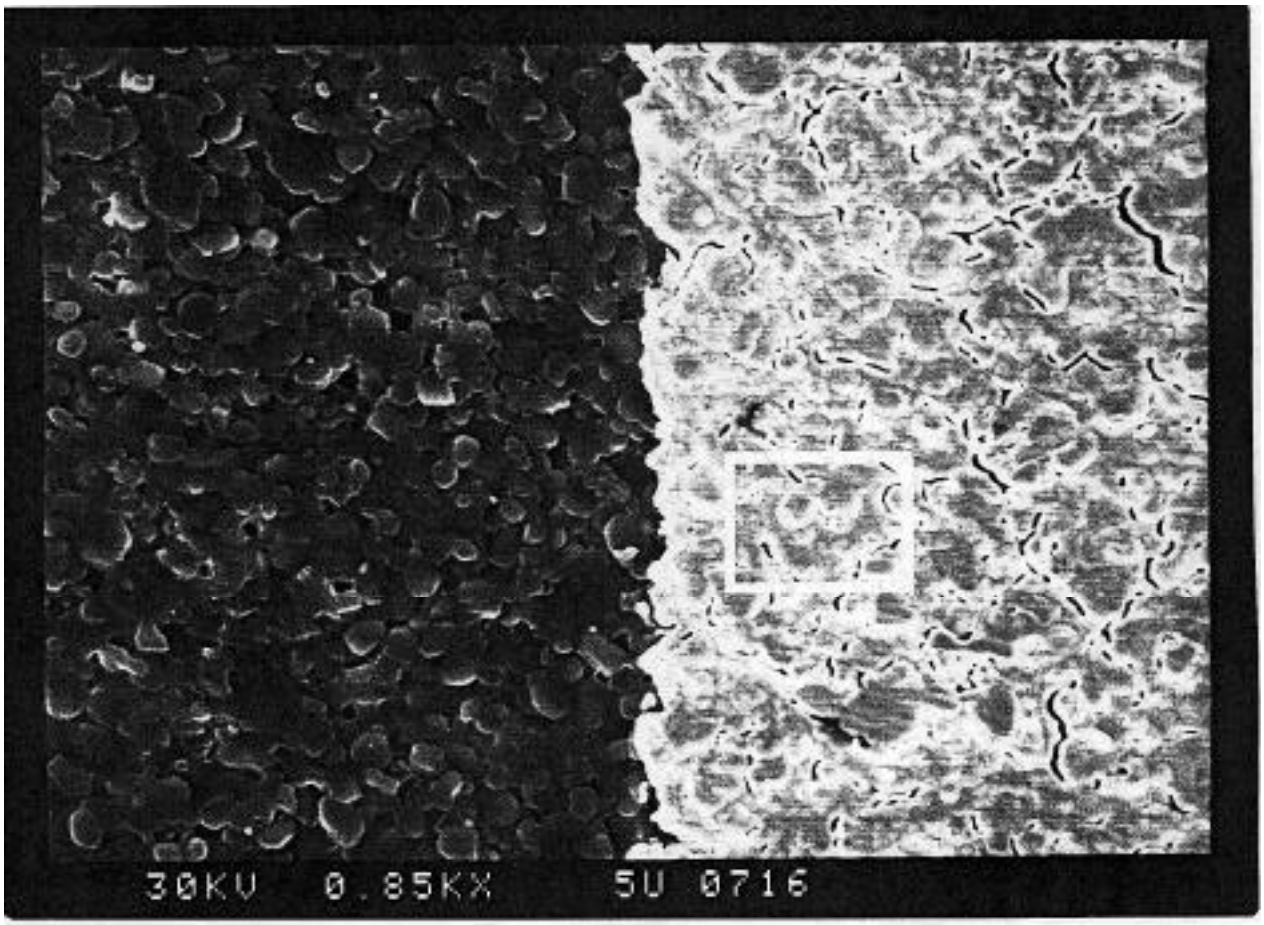
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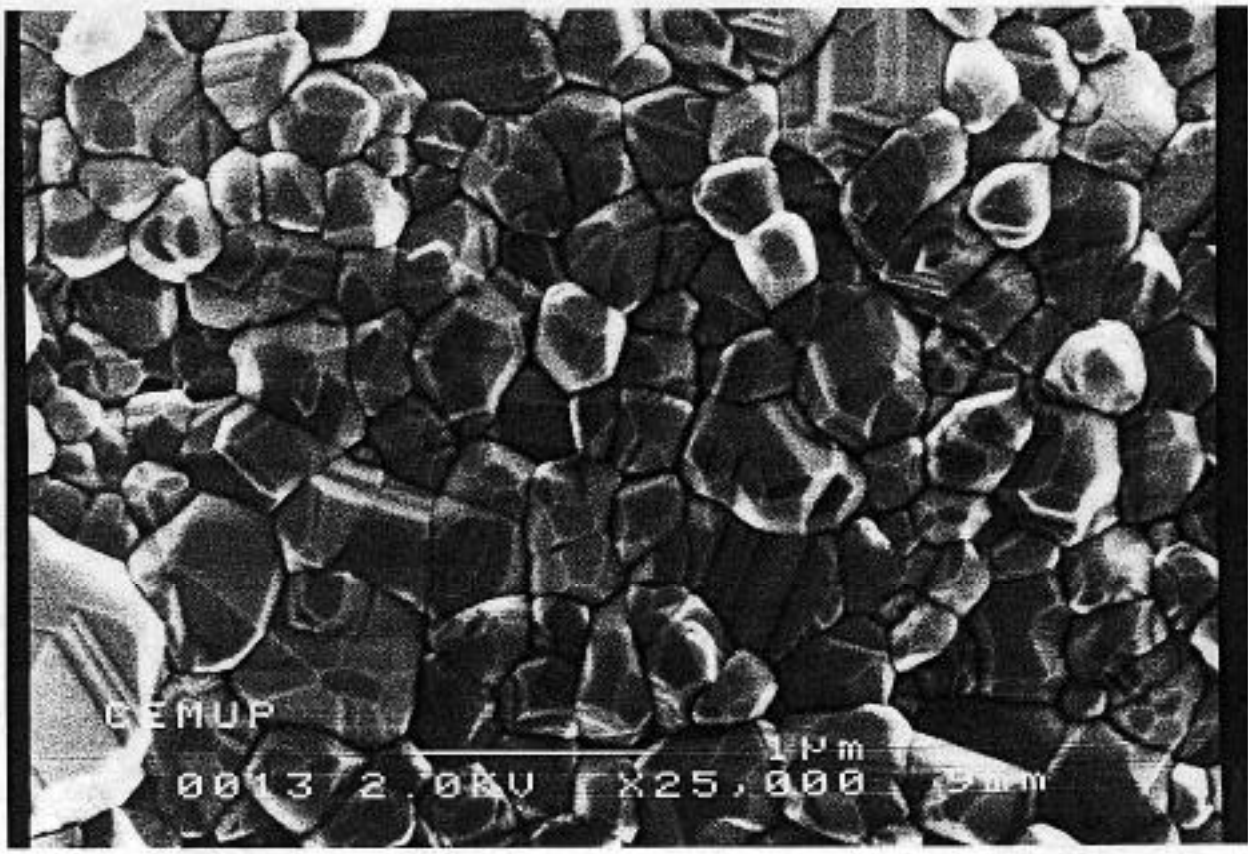
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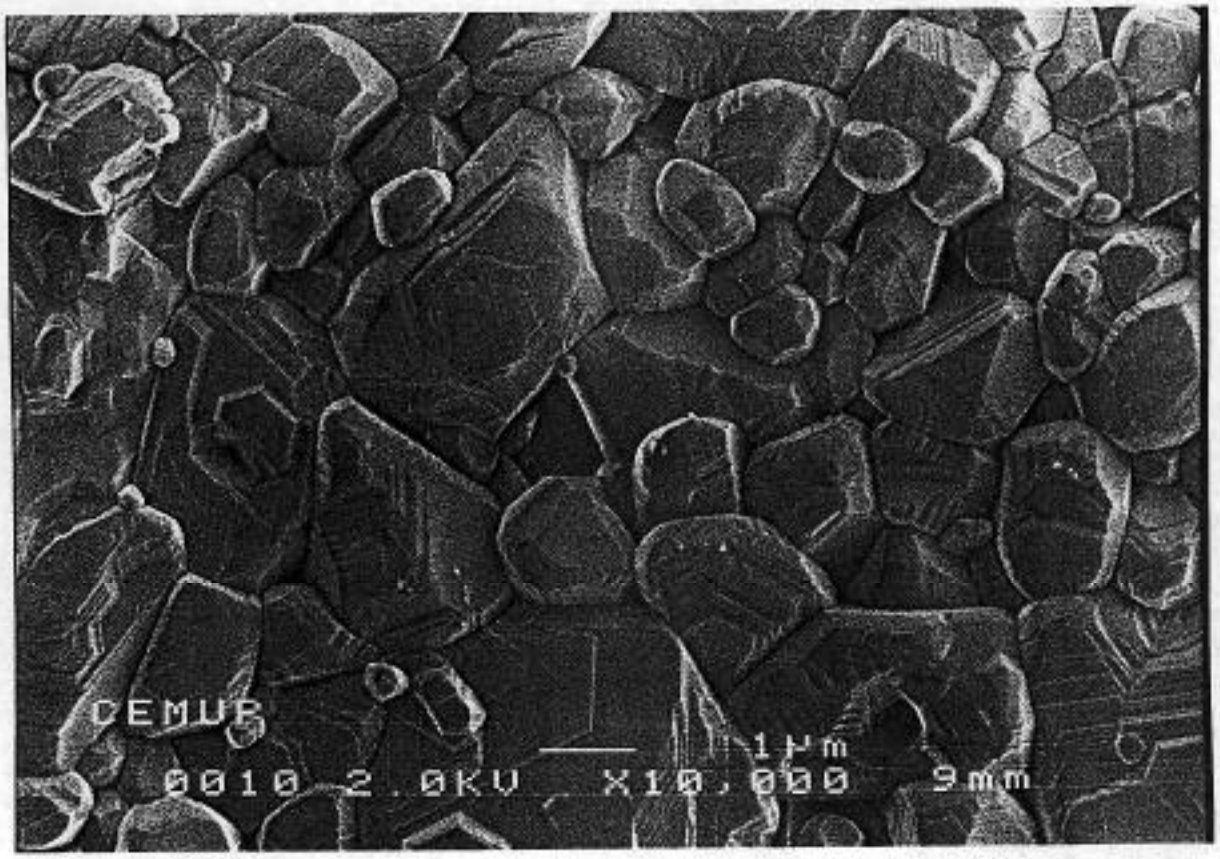
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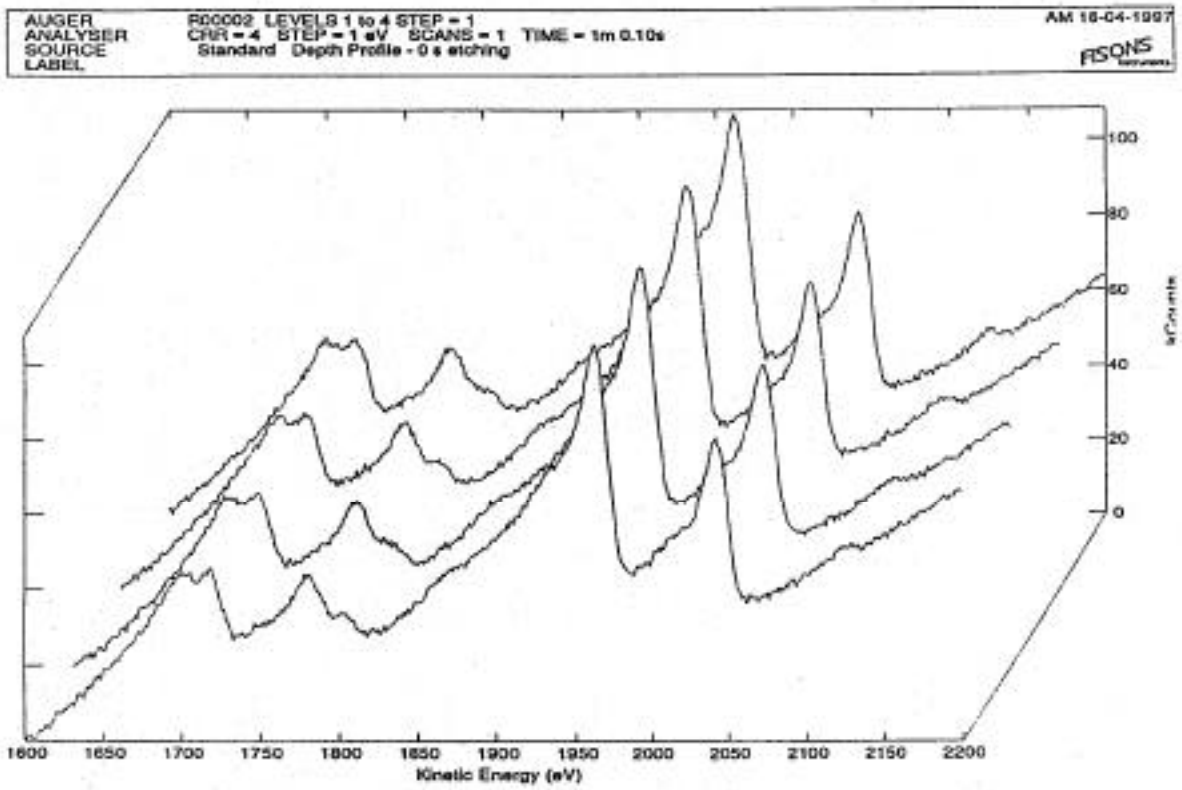
AUGER
ANALYSER
SOURCE
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CRR = 4 STEP = 1 eV SCANS = 1 TIME = 1m 0.10s
Standard Depth Profile - 0 s etching
AM 16-04-1997
FISONS
100
80
60
40
20
0
1600
1650
1700
1750
1800
1850
1900
1950
2000
2050
2100
2150
2200
Kinetic Energy (eV)