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Thin-Film Characterization for High-Temperature Applications[1]

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Most thin films produced by a wide variety of methods, either physical or chemical (PVD, CVD, sputtering, etc.) for temperature sensor applications, can be used only in very narrow ranges of temperatures, where their components are not subjected to differential thermal expansions, recrystallizations, and grain size modifications. This paper reports the production and characterization of thin films of platinum and titanium in ceramic substrates by one of the physical vapor deposition techniques, the e-gun evaporation. The choice of materials and the determination of film thickness, density, electrical resistivity, surface roughness, and structural characterization (X-ray, SEM, and AES) are studied. Special emphasis is given to the thermal and electrical behavior of these films between room temperature and 1000°C.

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

1. INTRODUCTION

Since Faraday first reported the vacuum deposition of a metal film in 1857 [1] using exploding wires and Nahrwold made the first use of thermal evaporation in vacuum to produce a thin film in 1887, the electron-beam

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evaporation technique has developed to a mature technology since 1972, offering now a vast range of applications.

The use of thin films for the construction of custom temperature sensors has received 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). There are also some drawbacks, such as the impossibility of reducing the size below a certain limit and the poor intrinsic temporal stability of some thin films. This constraint 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 evolutionary processes in thin films [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 stresses that put the film in tension or in compression. 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 behavior at high temperatures play a very important role in various aspects of the electronic industry [3]. The thermal sensors described here are of the thin-metal-film type, consisting of a substrate and thin- film layers deposited on it. Figure 1 shows a schematic drawing of the sensor.

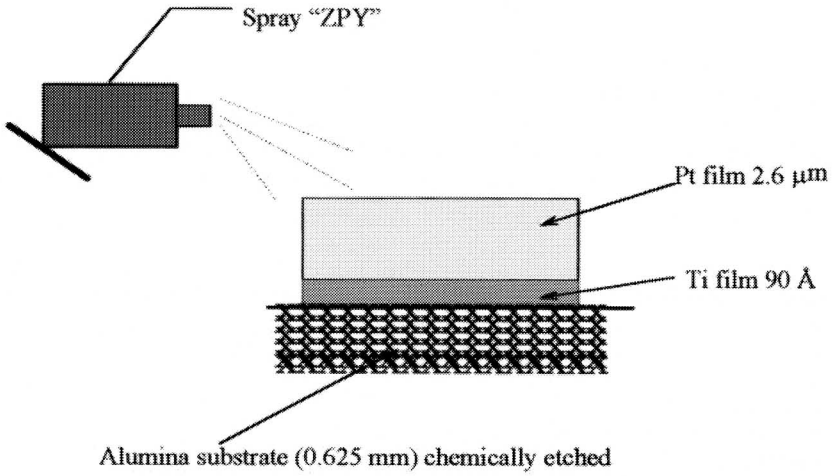

Fig. 1. Schematic diagram of the thermal sensor.

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 on 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 vapor deposition (PVD) film can be attributed to the film formation process. The advantage 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.

In the design of the sensors presented here, first we tried, to select and optimize the geometrical design by using photolithography and chemical etching. Second, we tried to select a substrate film/material combination (high-quality alumina substrate/platinum) to obtain reproducible results for sensor response [4] and to improve surface cleanliness of the substrate to enhance film adhesion. Finally, we tried to produce platinum electrical leads/platinum film contacts to decrease the thermoelectric effects at high temperature and, consequently, the electrical noise present. Table I shows the recommended substrate properties that we have tried to achieve.

Immediately after production, the thin films exhibit a large resistance associated with a large number of structural defects. These defects can be partially eliminated by carefully designed heat treatment of the ensemble substrate/film, decreasing the resistivity to a minimum, at a temperature depending on the film thickness [2]. As an example, a typical resistance change of platinum sensors during prolonged exposure at high temperature after proper aging is smaller than 0.2% for 2000 h at 350°C and smaller than 0.05% for 2000 h at 600°C [2].

The produced structure has some porosity, and the film has a columnar structure with closed and open voids and pinholes. As a consequence, the film density is lower than that of the bulk material, and the surface area exposed to ambient is much higher than at the geometrical surface area. These facts influence many film properties, such as hardness, deformation, chemical etching rate, resistivity, and index of reflection. Tensile stress can

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	Prevents outgassing
Mechanical strength	Prevents breakage
Matched thermal expansion	Prevents film stresses
Resistance to thermal shock	Prevents fractures
Chemical inertness	Permits contact with solvents

be produced 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 "microvoids" causes the tensile stresses.

2. EXPERIMENTAL PROCEDURE

The chemical etching of the alumina substrates was produced using a mixture of a 30% solution of ammonia in water, H_2O_2–130 vol and deionized water (1:1:5 in volume) for 5 min at 30°C.

On an alumina substrate (Rubalit 99.6% Al_2O_3 by Hoechst CeramTec), a titanium layer of 100 Å (hexagonal prisms of 99.99% Ti by Balzers) and platinum strips (99.99% Pt disk by Balzers) were deposited at room temperature, at an average rate of 10 Å $\cdot$ s^{-1}. Details of the masking processes and deposition of the metal film can be found in 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 of about 110 μm and thicknesses of 1.0 and 2.6 μm [7]. The thickness of the platinum strips was determined using a surface texture analysis system, Dektak 3030 (horizontal resolution, $\geqslant 0.25$ μm; vertical resolution, $\geqslant 0.01$ μm). The electrical leads were obtained by thermal compression of 0.135-mm-diameter platinum wire in a furnace (Carbolite HTC 16/8, with a Eurotherm temperature controller, Model 808P) up to 1180°C in air for 30 min. An insulation spray coating layer about 80 μm thick (ZYP product, alumina-based) was deposited above the platinum thin film in order to protect it from the environment.

Several measurements and tests were performed on the substrate/film deposit: electrical resistivity, resistance calibration, thermal stability, and structural, morphological, and chemical characterization (X-ray, SEM, and AES). The resistance of the film was measured with a Keithley 236 multimeter, appropriate for four-point measurements with 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 25-Ω platinum resistance thermometer (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 (Mettler balance PM1200; ± 0.0001 g) to the substrate films (rectangular sample, 2.5×6.0 cm) before and after the platinum deposition (2.36 μm thick). X-ray diffraction was used to characterize the alumina substrate and the platinum thin film. Both faces of the alumina substrate were also observed using a Philips difractometer PW

1730 equipped with a graphite monochromator for CuK_α (40-kV, 30-mA) radiation.

The SEM photographs for the morphological characterization were obtained in a JEOL–JSM 6301F. The AES spectra used for the platinum thin film chemical characterization 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 beam, spatial resolution $\cong 100$ nm.

3. RESULTS AND DISCUSSION

3.1. Electrical Resistivity and Resistance

The resistivity was measured in air after each step of the heat treatment. The heat treatment started at 100°C in steps of 100°C for 1 h, up to 1400°C. After each step the sample was allowed to cool to room temperature and 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 thicknesses, $\varepsilon = 1.0$ and $2.62\,\mu$m,[6] width $w = 126\,\mu$m, and length $l = 51$ mm.[7] 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. The resistivity of the film with a thickness of $1\,\mu$m increased by a factor of two from 900°C upward, but it vaporized at 1300°C. The resistivity of the sensor with a thickness of $2.62\,\mu$m reached a plateau between 1000 and 1200°C, and future annealing processes will be made up to the latter temperature. After this treatment the sensors maintain the resistivity values, around $1.43 \times 10^{-7}\,\Omega \cdot$ 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 and 1200°C, assuming that no further contraction of the thickness of the film occurred, we obtain a value of the resistivity of around $1.08 \times 10^{-7}\,\Omega \cdot$ m, very close to the accepted value at 22°C ($1.042 \times 10^{-7}\,\Omega \cdot$ m) [11]. This result suggests that after the heat treatment at 1200°C, the platinum film resistivity changes slightly, but within tolerable limits. As the resistance of each sensor as a function of temperature has to be known to obtain the temperature field in it, surrounded by

[6] Values measured before the heat treatment. Measurements on the 2.62-μm sensor after the heat treatments at 400 and 800°C showed a decrease in thickness to 2.14 and 1.99 μm, respectively.

[7] No changes in width or length were found after the heat treatments.

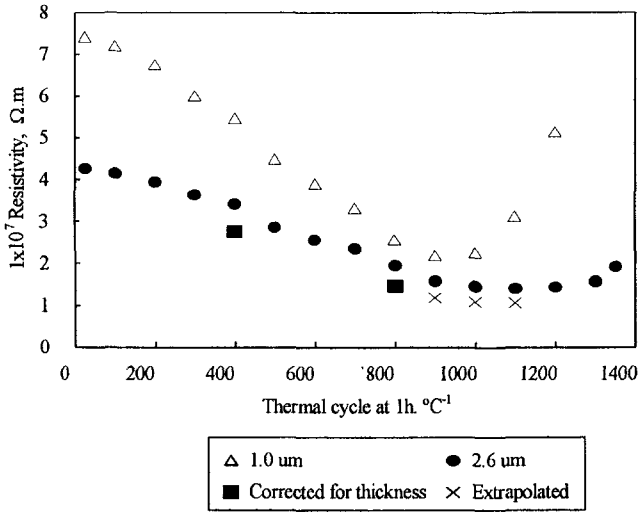

Fig. 2. Variation of the resistivity of the platinum strip with the heat treatments, for two strips with widths of 1 and 2.6 μm. The extrapolation is explained in the text.

different materials, these changes can be measured *in situ* and accounted for.

The stability of the resistance of the strip after the heat treatment and soldering process is very good, as the values at room temperature stay about the same. The resistance at room temperature before the heat treatment was approximately 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, agree to within 3% [7]. This is an advantage of the PVD technique for the manufacture of sensors and a necessary condition for accurate applications.

3.2. Calibration Resistance vs Temperature

Any transient 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 from simultaneous measurement of resistance and temperature. Figure 3 shows the calibration of one of the sensors over a wide range of temperature, 298 to 1273 K. The data were correlated using an equation of the form

$$R = R_0[1 + A(T - 273.15) + B(T - 273.15)^2 + C(T - 273.15)^3] \quad (1)$$

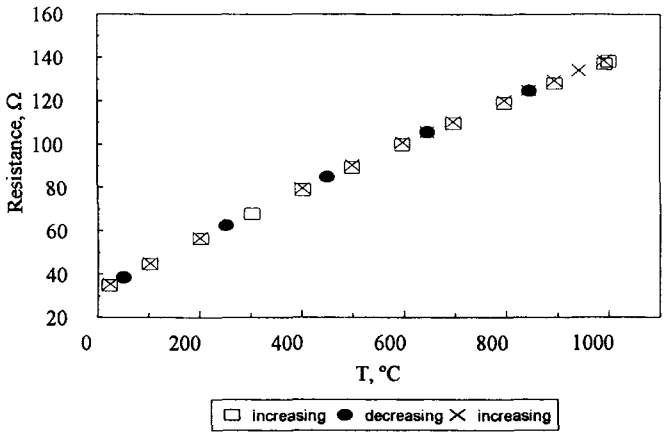

Fig. 3. Resistance calibration vs temperature for the platinum thin-film thermal sensor.

The result obtained was

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

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 were obtained going up, down, and up again in temperature. The deviations of the experimental points from Eq. (1) are shown in Fig. 4, and are, in general, within $\pm 0.1\%$. Table II presents the values obtained for A, B, and C as well as the common values encountered in the platinum resistance thermometers. The value of the temperature coefficient of resistance of the platinum strip in this range was found to be $A = 3.9164 \times 10^{-3}\ \mathrm{K}^{-1}$, with an uncertainty of $0.018214 \times 10^{-3}\ \mathrm{K}^{-1}$. This value falls between 3.908×10^{-3} and $3.9289 \times 10^{-3}\ \mathrm{K}^{-1}$, recommended for Type I platinum resistance thermometers in the range 273 to 1123 K, for very pure and well annealed platinum in the same range of temperature [10, 11]. This result supports the value of the resistivity obtained in the previous section. Since this coefficient is very sensitive to platinum purity and the annealing process, this result indicates that the platinum film produced by vapor deposition is very pure and of sufficient thickness to have normal bulk electrical properties.

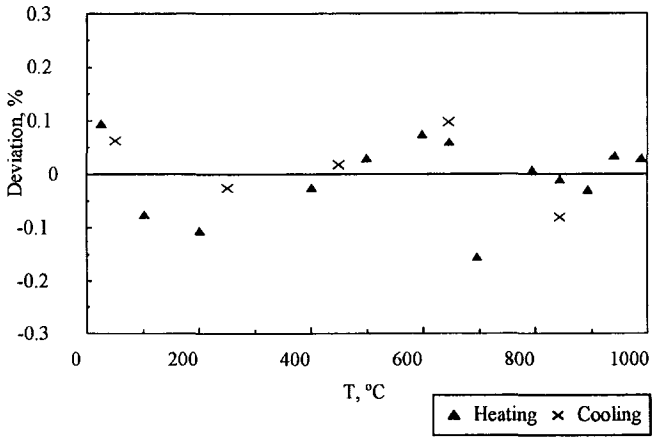

Fig. 4. Percentage deviation of the experimental measurements of the resistance of the thermal sensor platinum thin film as a function of temperature.

3.3. Density of the Platinum Thin Film

After heat treatment up to 800°C, the density of the platinum thin film was determined by a weighing method described in Section 2, with an uncertainty better than 0.1%, the main source of uncertainty being the film thickness ($\pm 0.01\ \mu$m). The measured value, 17,185 $kg \cdot m^{-3}$, is 20% lower than the density of bulk platinum (21,500 $kg \cdot m^{-3}$) [9].

3.4. Structural, Morphological, and Chemical Characterization

X-ray diffraction was used to characterize the alumina substrates and the platinum thin films. Both faces of the alumina were observed, and the lattice parameters, a and c, agreed with the values tabulated for α-Al_2O_3 [12] and Pt [13] to within 0.02%, given in Table III.

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 ($\pm$0.018214)	−7.1311 ($\pm$0.4257)	9.8795 ($\pm$2.7491)	1.3846
3.90802[a]	−5.8020[a]	—	1.3850[a]

[a] Type I, Platinum resistance thermometers, 0–850°C [10].

Table III. Lattice Parameters for α-Al_2O_3 and Pt; a and c Are the Lattice Parameters

α-Al_2O_3	Experimental	Ref. 12	Pt	Experimental	Ref. 13
a	4.7582	4.758	a	3.9208	3.9231
c	12.9915	12.991	c	3.9208	3.9231

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 platinum film surface was smoothed by the treatment, showing some small pinholes in the film. The grain size and texture after treatment are very similar to those of the original substrate. Preliminary depositions showed that better adhesion between the platinum film and the alumina was achieved using a 90- to 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, which is found to adhere well to both the alumina substrate and the platinum film.

Spectra performed using auger electron spectroscopy proved that the platinum surface is more than 99.99% pure. A standard profile is shown in

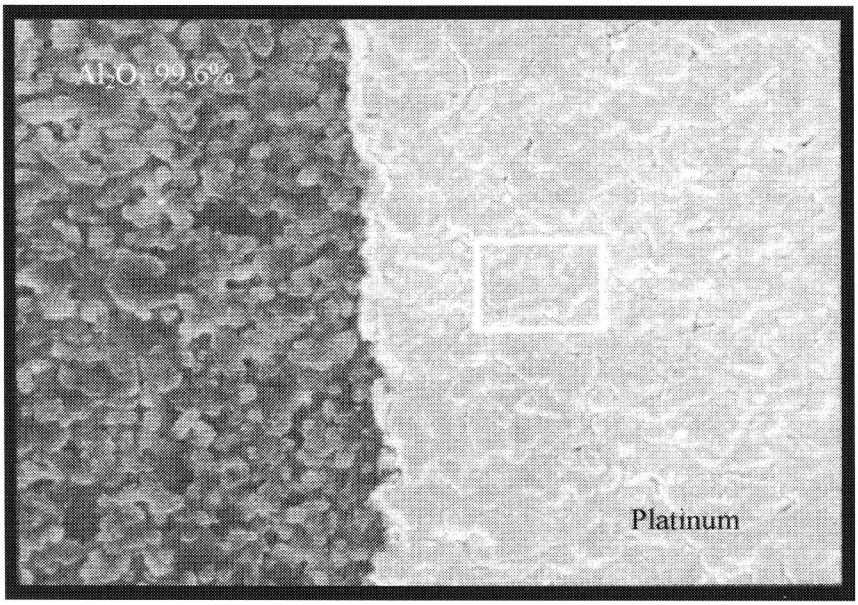

Fig. 5. SEM photograph of specific zones of the thermal sensor show the alumina (black)/ platinum (white) separation, before the heat treatment.

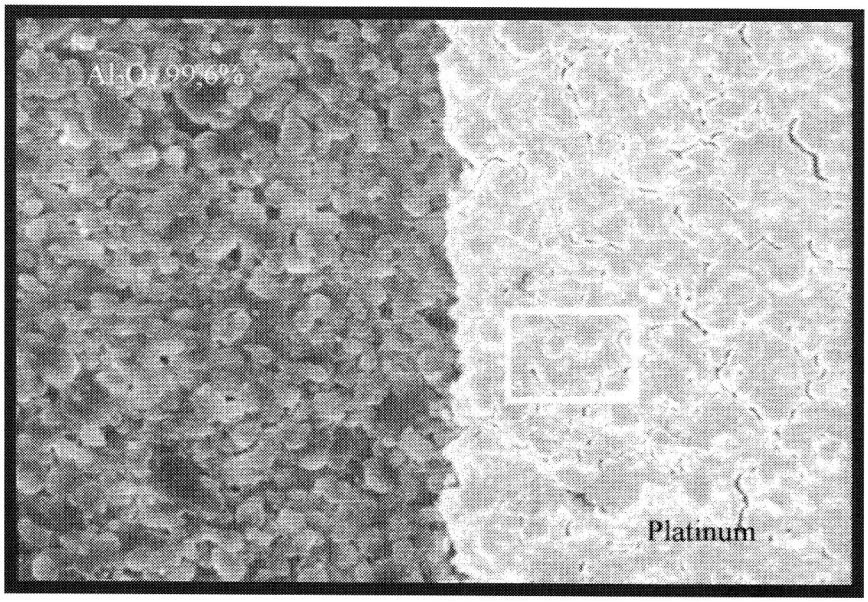

Fig. 6. SEM photograph of specific zones of the thermal sensor show the alumina (black)/ platinum (white) separation, after the heat treatment up to 1200°C.

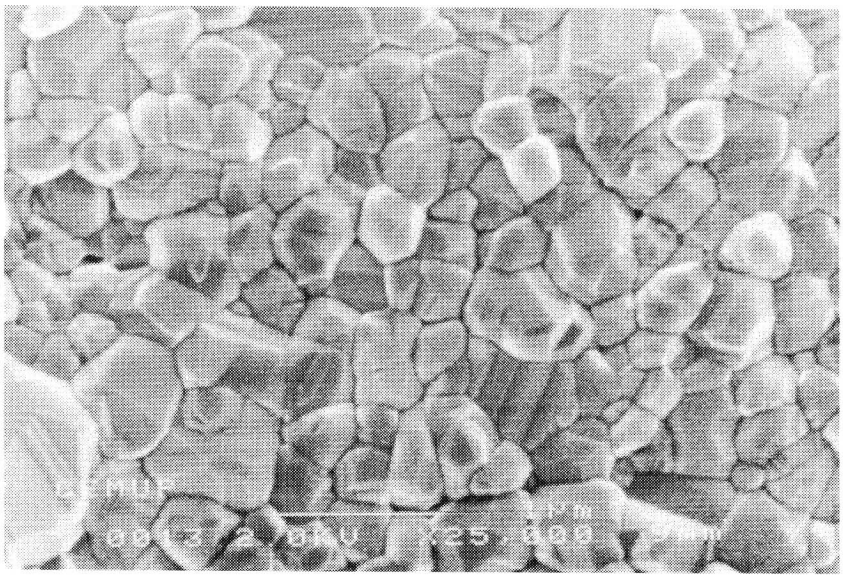

Fig. 7. SEM photograph of the thin layer of titanium (90 to 100 A).

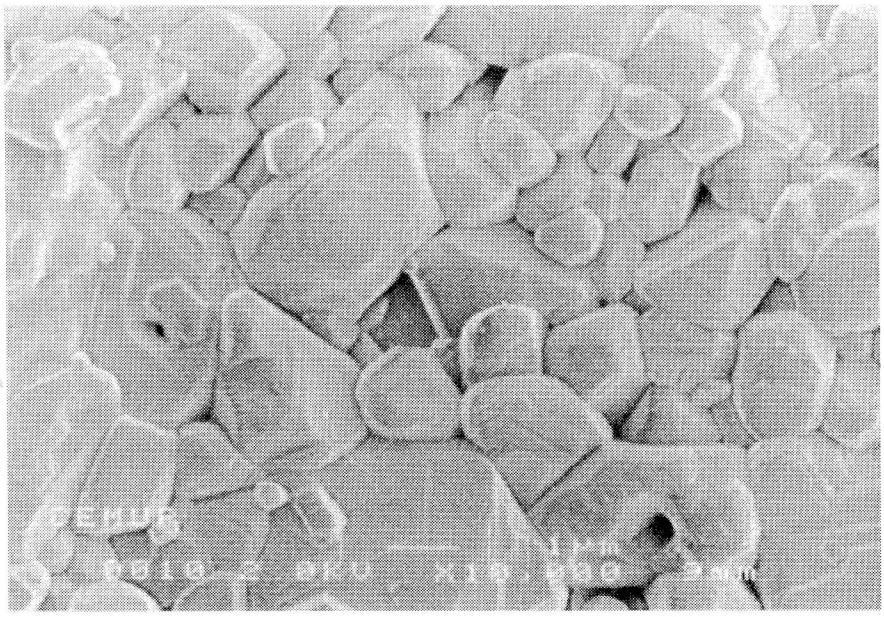

Fig. 8. SEM photograph of alumina substrate after chemical etching.

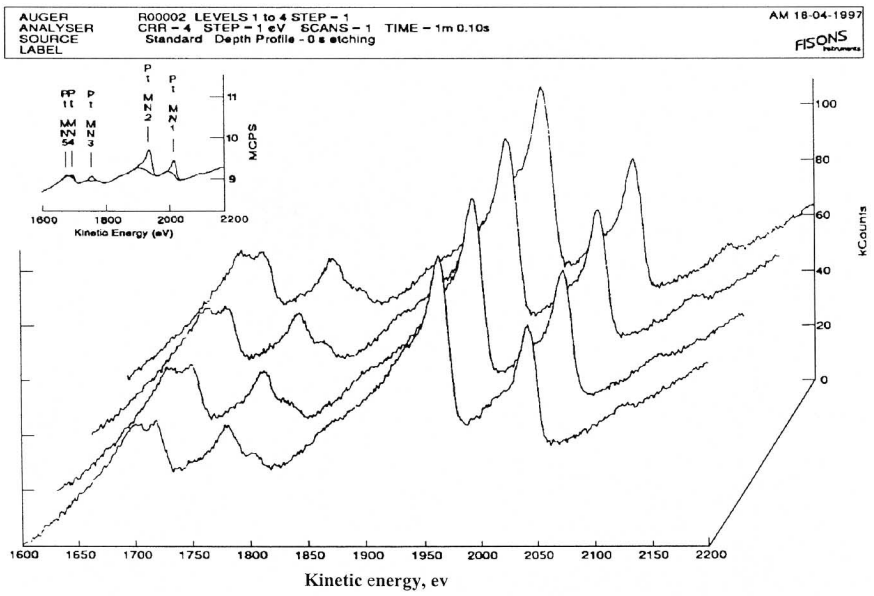

Fig. 9. Auger spectra for platinum thin film. The inset identifies the different peaks.

Fig. 9. Further tests for depth profiles by AES and XPS in a full cross section of a 1-μm film are under progress and will be reported soon, following a similar study on Ti/Al_2O_3 interfaces by Lu et al. [15].

4. CONCLUSION

This paper reports the construction and characterization of thermal sensors produced by vapor deposition techniques. The first prototypes show that the platinum deposited in the strip is highly pure, maintaining the properties of the bulk material, except density, such as the lattice parameters, the resistivity, and the thermal coefficient of resistance; only the density is significantly different. The heat treatment of the film produces, after several cycles, a very stable and constant resistivity. The platinum strip adheres strongly to the titanium layer and thus to the alumina substrate.

From the observed properties, the sensors, being electrically insulated, can be applied to measure temperature profiles or thermophysical properties of materials at high temperatures. In future work we will attempt to miniaturize this type of sensor for electronic applications down to the dimensions where the desired characteristics are maintained.

This work represents a necessary first step imposed by our primary objective of developing a new instrument to measure thermophysical properties of molten materials at high temperatures[8] [7]. This will be done by monitoring the temperature profile at the surface of the platinum thin film, as a function of time, when immersed in a melt.

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