

Some Observations on Laser Trimming Platinum Thin Films

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Platinum resistance thermometers have been selected for use as the basic instrument to define and reproduce the International Temperature Scale (ITS-90) (1, 2). The upper limit of the temperature region which they define has increased by some 300°C when compared to the previous International Temperature Scale, IPTS-68. On the ITS-90 scale the upper limit is defined by the freezing point of silver, 961.78°C. Thin film platinum sensors have demonstrated that they are able to meet the requirements of industrial operation, but ITS-90 has underlined their shortcomings, and improvements to production processes are required in order to enhance their performance, if ITS-90 is to be approached.

Thin Film Preparation

Thin film sensors are usually produced by the deposition of platinum onto a suitable substrate. In order to avoid any problems that might arise at the interface between the platinum layer and the substrate, the following criteria have to be taken into account (3):

- [a] Mismatch between the lattices must be less than ± 0.2 per cent
- [b] Differences in the coefficients of thermal expansion must be less than 20 per cent
- [c] There must be stability at the chemical interface. This means that the material which is selected for the substrate must not react chemically with the platinum layer.

Since the coefficients of thermal expansion of platinum and polycrystalline alumina are almost equal, being $7 \times 10^{-6}/\text{K}$ over the temperature range 50 to 300 K (4), alumina was chosen as the substrate for these sensors.

The production technology has been described elsewhere (5). Platinum layers were deposited, at 580 K, by magnetron sputtering of a plat-

inum target onto alumina substrates. The meander shape was then drawn by laser evaporation of the layer, using a pulsed Q-modulated Nd:YAG laser ($\lambda = 1.06 \mu\text{m}$) with pulse repetition rate of 20 Hz and train energy (for 10 pulses in a train) of 50 to 60 mJ. This technique is faster and more cost effective, and avoids the mask writing and chemical treatment that are necessary for lithographic patterning.

However, laser treatment of the layer parameters is not controllable, and so the final characteristics of the layer cannot be predicted.

Temperature/Resistance Values of the Layer

An assessment of the purity of the platinum target was made in accordance with ITS-90. It was found that the resistance ratio at the boiling point of water, $W(\text{H}_2\text{O b.p.}) > 1.3927$ ($W = R_{100^\circ\text{C}}/R_{0^\circ\text{C}}$, where R is the electrical resistance of the platinum layer). However, contrary to this, the sensors that were produced had a resistance ratio $W(\text{H}_2\text{O b.p.}) = 1.385$. In addition the resistance ratio at 4.2 K, $W = R_{4.2\text{K}}/R_{0^\circ\text{C}}$ was about 10^{-2} , which is two orders of magnitude greater than that proposed by ITS-90 for the most accurate thermometers.

An earlier investigation with this type of sensor showed that they required individual calibration in order to achieve an accuracy of ± 10 mK (6). The results for the percentage variation of the resistance with temperature for two typical sputtered platinum/alumina sensors, prepared by the same method, serial numbers 023 and 028, are presented in the Table. Their behaviour is characteristic of this type of sensor.

The sensors show significant differences in their values for resistance below 50 K. This can be explained (via Matthiessen's rule) by any

Resistance/Temperature Dependence from 5 to 270 K for Two Sputtered Laser Treated Sensors and Percentage Variation of their Resistance			
Temperature, K ± 3 mK	Resistance, ohms		ΔR , per cent
	023	028	
5.010	0.6456	1.6468	60.80
9.911	0.6788	1.6797	59.60
14.994	0.8048	1.8141	55.60
20.009	1.0989	2.1275	48.30
30.014	2.4391	3.4973	30.30
39.997	4.9082	5.9474	17.50
50.006	8.2700	9.2608	10.70
60.018	12.1720	13.1070	7.13
65.022	14.2278	15.1358	6.00
70.026	16.3411	17.2225	5.12
80.003	20.6053	21.4469	3.92
100.017	29.2092	29.9602	2.51
150.018	50.1719	50.7271	1.09
200.034	70.4822	70.8459	0.51
240.017	86.4281	86.6378	0.24
270.017	98.2334	98.3117	0.08

residual relative resistance. However, there is no reason to suppose that there are any impurities present in the layer during the platinum deposition process.

Eleven sensors of the same type were repeatedly subjected to thermal cycling between 60 to 320 K, and measurements of resistance were taken at 48 temperature points during every cycle. A visible shift in the temperature/resistance, $T(R)$, function was observed up to the sixteenth cycle and only after 20 cycles was saturation achieved. These results may be due to both the laser processing of the layer during fabrication of the meander shape and/or to interaction between the layer and the substrate. The effects of the laser processing can be observed by scanning electron microscopy (SEM).

Effects of the Laser Treatment

A SEM micrograph of a part of sensor 028 is shown in Figure 1(a). The sensor was covered with a glass frit to isolate the layer electrically. However, where the glass frit acted as an electrical isolator the SEM micrographs of the

platinum layer were spoilt. Therefore the cover was removed, but small amounts of glass frit which had been deposited in the laser-drawn lines still remained. For this reason, in Figures 1(a) to (d), lighter (white) lines appear on part of the sensor.

Thus laser treatment of the sensors appears to create some problems. First, the rough edges of the treated layer are clearly visible; these cause a reduction in the cross-sectional area of the platinum film. In Figure 1(b), which has twice the resolution of Figure 1(a), it can be seen that in some places the dimensions of the vertical cross section have become too small. Any mechanical tensions which have arisen as a result of the high temperature laser treatment will be increased in these cross-sectional areas and affect the temperature/resistance ratio.

During laser patterning evaporated material is redeposited onto the nearby film; this is shown by the spots in Figure 1(c). Some of these drops have dimensions equal to the width of the meander line layer, see Figure 1(d). It is therefore important to know both the structure and the

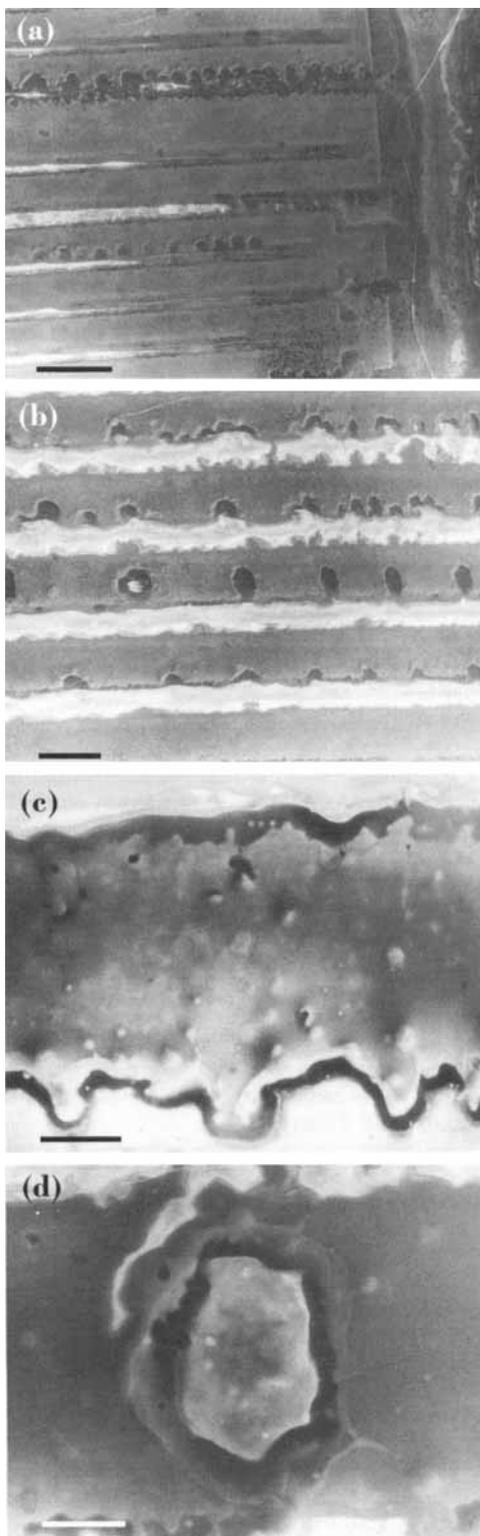


Fig. 1 (a) Scanning electron micrograph of sensor 028 showing lines of platinum deposited on alumina. The white lines are glass frit
 (b) The vertical cross-section of the platinum is reduced during laser processing
 (c) Drops of material from evaporation are redeposited onto nearby film
 (d) The size of the deposited drop is almost the same as the width of a meander line

composition of the drops, but this analysis is made difficult by the narrowness of the layers. If the drop is predominantly composed of alumina the stress will be larger, since alumina vaporises at a higher temperature than platinum. However, as a result of the large temperature difference between each drop and the layer on which it is deposited, strong mechanical tensions will occur in the cross section, causing the platinum lattice to become overstrained. It is suggested therefore that the electrical properties of the layer in this section become the determining ones for the sensor.

Some of these defects could be avoided if techniques used in the preparation of high transition temperature superconducting films (7) were employed. The film could, for example, be covered with photoresist prior to laser treatment and any redeposited material can then be removed by dissolving the resist in ethanol.

To sum up, we have found that the T(R) function in thin film platinum sensors used for temperature measurement is affected in an uncontrollable manner by laser treatment of the layer. Changes in the meander shape are caused by laser processing.

For this reason sensors fabricated by this method display a non-uniform temperature/resistance dependence. It is also suggested that due to the diffusion of aluminium atoms into the platinum lattice, changes in the electrical properties of the layer may also take place.

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References

- 1 "Suppl. Inf. for the Int. Temp. Scale of 1990", BIPM, 1990, Sevres, from BIPM Proc.-Verb. Com. Int. Poids et Mesures, 1989, 57, T1-21
- 2 B. L. Wibberley, *Platinum Metals Rev.*, 1989, 33, (3), 128
- 3 H. J. Scheel, M. Berkowski and B. Chabot, *Physica C*, 1991, 185-189, 2095
- 4 Handbook "Physicheskie Velichini" (Russ. Edn.), eds. I. S. Grigoriev and E. Z. Meiliov, Moscow, Energoatomizdat, 1991, ISBN 5-283-04013-5
- 5 D. A. Dimitrov, B. M. Terzijska, V. Guevezov and V. T. Kovachev, *Cryogenics*, 1990, 30, (4), 348
- 6 D. A. Dimitrov, A. L. Zahariev, J. K. Georgiev, G. A. Kolev, J. N. Petrinski and T. Ivanov, *Cryogenics*, 1994, 34, (6), 487
- 7 J. Mannhart, M. Scheuetmann, C. C. Tsuei, M. M. Oprysko, C. C. Chi, C. P. Umbach, R. H. Koch and C. Miller, *Appl. Phys. Lett.*, 1988, 52, (15), 1271

Iridium Microelectrode for Testing Water Quality

The lack of sound environmental management of our natural resources is of growing concern, and increasingly legislation is setting standards for the pollutants which can be released into the environment. Pollution in river water, however, is now routinely checked, and improving the quality of the water into which industrial and domestic effluent may be discharged is one aim of the national River Authorities.

Water is tested for the presence and quantity of many different types of pollutants, including organic pollutants, such as pesticides and insecticides, nitrates and nitrites, and the elements, such as the heavy metals: lead, cadmium and copper. A number of analytical techniques are presently used to measure the amounts of around 6000 individual pollutants, mainly by laboratory analysis from collected samples.

However, an advance on the technique for monitoring lead and cadmium using an improved mercury-based iridium microelectrode is suggested in a paper from the University of Geneva (M.-L. Tercier, N. Parthasarathy and J. Buffle, *Electroanalysis*, 1995, 7, (1), 55-63).

The drawbacks to using microelectrodes for water analysis have been a lack of reproducibility in their fabrication and the difficulty in characterising them, and since complete reliability is necessary in the analysis of water contaminants, microelectrodes have not been used. However, based on prior research on ultramicroelectrodes, the researchers have produced a sturdily constructed, reliable mercury-plated iridium-based microelectrode, having a central iridium electrode of radius 62 μm , which gives reproducible results. This has been achieved by thorough attention to all aspects of the fabrication process, in particular, since the electrode is built within a glass pipette, to the iridium-glass sealing, and to the iridium-copper soldering in order to obtain perfect electrical contact. The morphology of the iridium disk is very important and strongly depends on using a reproducible standard polishing procedure.

Optimal polishing procedures and conditions are given to achieve this. The build up of electrostatic charge on the tip of the microelectrode is avoided by shielding the glass pipette with an outer layer of palladium.

To date the system has achieved near 100 per cent reproducibility and reliability for the measurement of trace metals by differential pulse anodic stripping voltammetry and square wave anodic stripping voltammetry (SWASV). Electrodes have been used continuously for several days without requiring a renewal of the mercury layer.

When tested using SWASV in river water, which contained a high level of suspended particle content, trace amounts of free cadmium and lead were able to be measured in concentrations as low as 0.5 nM and 0.1 nM, respectively. Direct SWASV measurements using such a microelectrode were the best for routine analysis of dissolved trace metals in fresh water, since problems caused by contamination and/or adsorption are minimised. This method allowed the free and total metal concentrations to be rapidly determined. These are the most important trace metal speciation parameters. Sample pretreatment is not required. At present the lifetime of these state-of-the-art microelectrodes is more than 2 years.

If dissolved organic matter in low concentrations of 1 to 2 mg/litre, relative to particle load, is present then trace metals at levels of 50 pM can be detected, although high levels of particles do not hinder SWASV measurements. To avoid problems in water with higher dissolved organic content and to extend the use of the sensor for *in situ* measurements of any type of natural water, a membrane coated microsensor is being developed. Other uses suggested for this sensor include an *in situ* automatic quality control system for industrial application, the measurements of samples of small volume, being used in still waters and as part of other routine detection systems.