The Platinum Metals in Electronics

KEY AREA FOR GROWTH AND NEW TECHNOLOGY

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The sophistication possible with modern electronic and microelectronic devices depends ultimately on the materials from which they are made. The platinum metals have assumed a vital role in electronics at every stage in its evolution. They are found in both thin and thick film devices which together constitute the backbone of electronic manufacturing technology and overall this area represents one of their main applications in terms of metal consumption.

The platinum metals have been associated with the electrical and electronics industries for almost as long as the metals themselves have been refined and fabricated. For many years it was their unsurpassed metallurgical properties that accounted for their widespread application, particularly in electrical contacts and in various electrode systems. However the 1970s, which saw the beginning of the microelectronics revolution, changed the need for the platinum metals but in no way made them redundant. Instead it opened up a range of new applications. For example, the need for low-current contacts gradually diminished as electronic switching progressed, but on the other hand the requirement for materials for the new microelectronic devices produced a high-technology impetus for the platinum metals. It is their use in electronics which is reviewed in this paper and an overview of the total picture is given by taking specific examples of their application; some are shown in Figure 1.

Current world demand data for the platinum metals in electronic applications is summarised in Figure 2. It shows that the commercially important metals are ruthenium and palladium, and that in both these cases microelectronics accounts for large percentages of individual demand. If broken down according to geographical region, the data show a bias towards ruthenium in Japan and towards palladium in the U.S.A. Although only 3 per cent of total demand for platinum itself is due to electronic applications, this still corresponds to several tonnes of metal. In this case the U.S.A. accounts for the majority of sales. Rhodium and iridium are involved mainly in ancillary applications such as crystal growing.

Present and Future Applications

The platinum metals are found in practically every facet of electronic technology and examples of their application are given in Table 1. Some of these have been commercially important for nearly twenty years while others are still at the research and development stage. The major electronic applications in terms of absolute metal consumption are undoubtedly thick film resistors, thick film conductors, multilayer ceramic capacitors (MLCCs) and connectors. The first accounts for the majority of ruthenium usage and the remainder for the majority of palladium usage. Connector technology—where palladium is used as a cost-effective substitute for gold—has been reviewed recently in this journal (1) and is therefore not discussed in this paper. Thin film technology offers the greatest diversity of applications for the platinum metals. They are found in all aspects of the technology from sensing to signal processing and display, and as they give rise to the basic response of the particular devices they are often irreplaceable. They are also widely used during the manufacture of electronic materials. For example, the accurate temperature control of
Fig. 1 This diverse collection of hardware illustrates a range of applications of the platinum metals in microelectronics. Among the devices shown are several multilayer ceramic capacitors incorporating palladium buried electrodes and palladium-silver end terminations, a resistor network with palladium-silver conductors and ruthenium-based resistors, hybrid structures containing palladium-silver and palladium-gold conductors and ruthenium-based resistors, as well as very large scale integrated circuits with platinum silicide Schottky contacts.

Fig. 2 The use of the platinum metals in electronic applications is shown here as a percentage of the total world demand in the year 1983.
### Table I
#### Present and Potential Applications of the Platinum Metals in Electronics

<table>
<thead>
<tr>
<th>THIN FILM TECHNOLOGY</th>
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<tbody>
<tr>
<td>Integrated circuits</td>
<td>Platinum silicide ohmic and Schottky contacts, on-chip capacitors</td>
</tr>
<tr>
<td>Data storage</td>
<td>Rhodium/RhSi optical media, osmium-doped magnetic tapes</td>
</tr>
<tr>
<td>Sensors</td>
<td>Palladium-gated MOSFETs, platinum/zirconia oxygen sensors, platinum temperature sensors</td>
</tr>
<tr>
<td>Displays</td>
<td>IrO₂ electrochromic displays, automatic dipping rear-view mirrors</td>
</tr>
</tbody>
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<table>
<thead>
<tr>
<th>THICK FILM TECHNOLOGY</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductors</td>
<td>Palladium-silver, palladium-gold, platinum-gold, platinum-palladium-silver, platinum</td>
</tr>
<tr>
<td>Resistors</td>
<td>RuO₂, Bi₂Ru₂O₇</td>
</tr>
<tr>
<td>Sensors</td>
<td>Platinum resistance thermometer</td>
</tr>
<tr>
<td>MULTILAYER CERAMIC CAPACITORS</td>
<td>Palladium, palladium-silver</td>
</tr>
<tr>
<td>CONNECTORS</td>
<td>Palladium alloys including palladium-nickel</td>
</tr>
<tr>
<td>MANUFACTURING</td>
<td>Thermocouples, platinum or iridium crucibles for crystal growing, glass melting equipment</td>
</tr>
<tr>
<td></td>
<td>for manufacture of optical fibres</td>
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</tbody>
</table>

Diffusion furnaces is accomplished using platinum metal thermocouples. High-purity single crystals of many specialised electronic materials including lithium niobate, gadolinium gallium garnet and yttrium aluminium garnet are grown from the melt and non-contaminating, heat resistant containment materials are required. Often the only satisfactory containers are crucibles made from the platinum metals—normally platinum, iridium or alloys thereof depending on the melting point of the particular oxide.

**Thin Film Technology**

Thin film technology involves the fabrication of circuits by vacuum deposition processes such as evaporation, chemical vapour deposition or sputtering. The process produces thin films of conductive, resistive, insulating or semiconducting materials, and allows active semiconductor devices as well as passive components to be fabricated at a circuit density orders-of-magnitude above any other technology. The main application areas of the platinum metals as thin films are sensing, display and integrated circuit (IC) technology. This section discusses the advantages of platinum metal silicides for both ICs and optical storage media and also describes various gas sensors and electrochromic displays.

There is great interest in the use of platinum silicide in silicon IC technology. As a metallisation material—for providing both ohmic low resistance contacts to silicon and rectifying contacts (Schottky diodes)—platinum silicide has low resistance and high stability in subsequent processing conditions. The material is particularly important in the fabrication of bipolar ICs where the metallisation is largely determined by the need to form Schottky diodes with stable and reproducible characteristics. The silicide layer is formed in situ by sputtering a thin platinum layer (~40 nm) onto the silicon surface followed by sintering at 650°C. Silicides of the platinum metals may be exploited in other ways, for example, exploratory work at I.B.M. has demonstrated that they could be used as long-term archival optical storage media; a low power laser being used to induce local silicide formation in a platinum metal-silicon bilayer structure. From the systems studied to date, rhodium-silicon appears to be the most promising due to its relatively low writing power and excellent archival properties. I.B.M. are also working on the use of platinum silicide conductors in complementary metal oxide
semiconductor (CMOS) structures (4) and thin film on-chip decoupling capacitors whose electrodes are based on platinum-refractory metal intermetallics (5).

Hydrogen-sensitive gas sensors, compatible with integrated circuit technology, can be made using platinum or palladium as the gate metal of a metal oxide semiconductor (MOS) transistor. Hydrogen molecules dissociate on the catalytic metal surface and diffuse through the thin metal film to the metal-insulator interface. Here the hydrogen atoms form a dipolar layer which produces a voltage drop and hence varies the characteristics of the MOS structure, see Figure 3. Lundström gives a detailed account of these devices, and shows that there is an equilibrium between the numbers of adsorbed hydrogen atoms on the surface and those at the interface (6). The number at the surface depends on the hydrogen partial pressure in the atmosphere and the presence of other gases. Hence the change in response can be calibrated to indicate the concentration of hydrogen present in the atmosphere. Detection limits for hydrogen in air are of the order of 0.5 ppm and proposed applications include leak detectors and fire alarm systems.

Several technical problems remain to be solved, particularly those related to long-term stability. These arise due to changes at the metal surface and metal-insulator interface, especially as a result of contamination and poisoning of the catalytic film. The structure of the film also has a marked effect on gas sensitivity and Lundström suggests there may be at least two types of palladium film produced by thermal evaporation. Sensors based on porous gate metals show much better selectivity to different gases with improved selectivity being observed with palladium and platinum themselves. Such developments should ensure an expanding use of the metals in integrated sensing devices.

The rapidly growing need for simple passive displays has created considerable interest in electrochromic displays (ECDs), principally due to their wide angle of view and low power consumption in low-switching-rate applications. Operationally an ECD is equivalent to a battery with a visible state of charge. When the display is fully charged, that is to say coloured, it passes no current either with the charging voltage connected or under open circuit. It therefore maintains its colour even when the power supply is switched off. ECDs are the only
highly developed display technology with non-volatile capabilities.

Tungsten trioxide is probably the leading electrochromic material, but its commercial development has been (and still is) hampered by technical problems. Of these, a low speed of response and time-dependent degradation in aqueous electrolytes are the most serious. Thin film deposited iridium oxide is an alternative electrochromic material which largely overcomes these problems, possessing better speed of response and greater stability than tungsten trioxide. The iridium oxide film is transparent in the "off" state but this quickly changes to blue-black when stimulated by a brief electrical pulse. Response time is reported to be 0.05 seconds, twenty times faster than tungsten trioxide and about the same as liquid crystal displays. A simple seven-segment iridium oxide ECD which can be driven with a simple, low power, battery-operated circuit and which could open the way for their commercial development has been reported from Bell Laboratories (7).

Electrochromic iridium oxide is also being considered for automatically dipping vehicle rear view mirrors to reduce glare during nighttime driving. When a sensor in the mirror registers flare of a certain intensity the electrochromic film is switched from colourless to blue-black, thereby reducing the reflectivity of the mirror. If this application were fully exploited, and iridium oxide is currently the material preferred by U.S.A. and Japanese manufacturers, it would open up a major new market for iridium.

Thick Film Technology

Thick film technology utilises screen printing techniques to deposit patterned resistive, conductive and insulating films to form miniature electronic components or circuits. The pastes (or inks) used consist of viscous dispersions of finely ground inorganic powders in organic liquids which exhibit pseudoplastic rheological properties under the various shear rates encountered during the screen printing process. In use the inks are deposited through a finely woven stainless steel mesh, onto which a pattern has been delineated, by the passage of a squeegee across the surface of the screen. The supporting substrate onto which the print is deposited is usually a 96 per cent alumina ceramic chosen primarily for its inertness and ability to withstand the multiple firing stages which follow paste deposition.

After deposition the print is allowed to settle for a few minutes before being dried at 100 to 150°C and then fired at between 600 and 1000°C. Although extremely stable devices are produced as a consequence of the firing process the reaction chemistry is extremely complex and in many cases only poorly understood. Hence very careful control of the physical and chemical properties of the starting materials, as well as accurate process control, are required to achieve consistent results.

The use of thick film materials is not restricted to a single segment of the microelectronics industry but rather covers a whole spectrum of applications ranging from simple chip resistors costing a few pence to complex multilayer hybrids costing many hundreds of pounds. Table II shows the constituents encountered in many of the commercial thick film formulations available for this wide range of applications and it can be seen that the platinum metals are of crucial importance as the functional phase of both the conductor and resistor inks.

In nearly every application of thick film technology the resistor material used is based upon a conductive phase of ruthenium in oxide or compound form. Although not unique in their properties, ruthenium(IV) compounds offer an ideal compromise in terms of high temperature oxidation resistance over base metal alternatives such as molybdenum(IV) and titanium(IV) compounds, and significant cost savings over competing conductive phases based upon compounds of iridium, rhodium and osmium.

It is especially significant that even in an industry such as electronics which is characterised by extremely high rates of technological change the use of ruthenium(IV)
compounds has persisted for over 15 years with little sign of being superseded. Although many base metal materials have been investigated (and in some cases brought to market) none have approached ruthenium(IV) based resistor materials in terms of electrical properties such as temperature coefficient of resistance (TCR) or long term stability.

A cross section through a fired thick film resistor is shown schematically in Figure 4. It can be seen that the ruthenium oxide is concentrated at the boundaries of the glass particles, forming a conductive chain inside an insulating glass matrix. The final electrical properties of the fired resistor are dependent not only upon the volume fraction of ruthenium dioxide present but also on the particle size and morphology of the conducting and insulating phases and the chemical nature of the glass matrix itself. In the firing process a complex series of high temperature chemical reactions occur during which the organic liquid burns off and the film sinters to a dense thick film. It is necessary to control rigorously processing parameters such as the firing cycle and firing atmosphere by the use of sophisticated multizone tunnel furnaces. Even so, fired resistance values often vary by as much as ±20 per cent in production, necessitating a final adjustment of the resistor value by cutting into the film with a laser or air abrasive trimmer.

For the more sophisticated applications of thick film such as high performance military

<table>
<thead>
<tr>
<th>FUNCTIONAL PHASE</th>
<th>Conductor</th>
<th>Resistor</th>
<th>Dielectric</th>
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<tbody>
<tr>
<td></td>
<td>Gold, platinum, platinum-gold</td>
<td>Bi$_3$Ru$_2$O$_7$</td>
<td>Glass</td>
</tr>
<tr>
<td></td>
<td>Silver, palladium-silver</td>
<td>RuO$_2$</td>
<td>Glassceramic</td>
</tr>
<tr>
<td></td>
<td>Platinum-palladium-silver</td>
<td></td>
<td>Glass/alumina</td>
</tr>
<tr>
<td></td>
<td>Copper, nickel, aluminium</td>
<td></td>
<td>(filled dielectrics)</td>
</tr>
</tbody>
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<table>
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<tr>
<th>BINDER</th>
<th>Borosilicate or aluminosilicate glasses</th>
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<tbody>
<tr>
<td>Fritted</td>
<td>CuO, CdO</td>
</tr>
<tr>
<td>Reactively bonded</td>
<td>Oxide/glass</td>
</tr>
<tr>
<td>Mixed bonded</td>
<td></td>
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<thead>
<tr>
<th>VEHICLE</th>
<th>Terpineol</th>
<th>Ethyl cellulose</th>
</tr>
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<tbody>
<tr>
<td>Volatile phase</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-volatile phase</td>
<td></td>
<td></td>
</tr>
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</table>

Fig. 4 The microstructures of fired thick film resistors and conductors are compared here. The ruthenium-based conductive chains built up inside an insulating glass matrix, which typify resistor systems, are illustrated on the left. Conductors, shown on the right, are thinner than resistors and have a much higher loading of the metallic conducting phase.
hybrids considerable use is made of minor additives such as niobium pentoxide, which interact with the conductive phase during the firing cycle to counteract any oxygen deficiency that may occur. This has the effect of altering not only the resistivity of the fired film but also improving electrical properties such as the TCR.

In moving from one extreme of the thick film applications spectrum to the other the constituents of the resistor pastes vary only marginally. In the case of conductors, however, significant alterations of the functional phase occur depending upon the technical requirements and price sensitivity of the application. Apart from their obvious function of providing low resistivity interconnections from point to point in a circuit, thick film conductors are also used for a variety of specialised purposes including terminations for screen printed resistors, pads for lead frame and device attachments, and pads for wire bonding connections to silicon circuitry.

Like resistor formulations, fritted conductor pastes consist of a functional phase of conducting particles in a glass matrix which is used to bond the metal particles to the surface of the alumina substrate on firing. As an aid to sintering and adhesion, fluxing agents such as bismuth oxide are often included even though this is now thought to cause problems by reducing conductor adhesion when soldered tracks are stored at elevated temperatures (8).

An alternative technique known as reactive bonding uses very low levels of metal oxides to form an alumina spinel at the metal-substrate interface at a higher than normal firing temperature (980°C). This bonding technique has the advantage of ensuring the highest possible electrical conductivity but occasionally suffers from problems, especially during low...
temperature refire when some of the oxides can migrate to the conductor surface and inhibit wire bonding (9). A third bonding technique, known as mixed bonding, uses a combination of the two techniques outlined above to provide improved conductivities and fewer aged adhesion or refire problems and appears to be gaining favour with both paste manufacturers and users.

The structures of fired thick film conductors and resistors are illustrated in Figure 4, which shows that the film thickness of the conductor is much less than that of the resistor and also the use of a very much higher loading of the metallic conducting phase. Although under or over firing will affect film conductivity and adhesion, and poor furnace atmospheres will result in solderability or wire bonding problems, the performance of platinum metal conductor systems is considerably less sensitive to process variations than the resistor materials. Base metal conductor systems such as copper or nickel which, for the most part, rely on neutral (nitrogen) or reducing (nitrogen/hydrogen) atmospheres are seriously degraded if the furnace atmosphere is contaminated with oxygen.

A binary composition of a platinum metal and silver, in particular palladium-silver, constitutes the basis of the most widely used thick film conductors. These conductors find wide application in the production of chip resistors, resistor networks and hybrids for industrial, automotive, telecommunications and even high-technology consumer applications such as video cassette recorders. The presence of palladium serves to inhibit solder leaching silver out of the conductor and it also reduces silver migration in hot or humid conditions, especially when high electric fields are present between closely adjacent conductor tracks held at different electric potentials.

For less stringent applications where cost is of great importance the ratio of silver to palladium can be as high as 12:1. For applications where higher reliability is required in adverse environments the ratio of silver to palladium is reduced to 1.85:1. Since any further decrease in the silver : palladium ratio leads to solderability problems and a reduction in electrical conductivity below acceptable levels, gold has for many years been the functional phase chosen for circuits demanding the highest performance and reliability. With the advent of ever more complex silicon circuitry associated with the move from large scale integration (LSI) to very large scale integration (VLSI) and the consequent difficulties associated with pretesting and burning in of the chip, the concept of a chip carrier surface mounted onto the substrate has arisen. Since gold readily dissolves in the tin-lead solders needed to attach the chip carriers to the top conductors of the circuit the use of special lead-indium solders and/or platinum-gold top conductors is becoming of increasing importance to the industry.

**Multilayer Ceramic Capacitors**

The capacitance of a simple discrete capacitor consisting of two metal electrodes separated by a dielectric is proportional to the electrode area. For a given dielectric material it is necessary to increase the electrode area in order to increase the overall capacitance obtainable. This is undesirable in microelectronic applications where the large areas required are incompatible with the size reductions associated with LSI and VLSI silicon technology. Multilayer ceramic capacitors (MLCCs) solve this problem by stacking alternate layers of electrode and dielectric, which are “terminated” to provide electrical connection to the electrodes. For a given plate area, the capacitance of a MLCC is proportional to the number of laminated dielectric layers. This monolithic multilayer construction, shown in Figure 5, provides a large electrode area in a small volume package.

The most common dielectric used in MLCC manufacture is barium titanate doped with a variety of oxides in order to alter its sintering characteristics and modify the electrical properties of the finished capacitor. The barium titanate is comminuted to a fine powder (roughly 3 µm diameter) and cast into a flexible
tape with the aid of a plasticiser and acrylic binder. The electrodes are then screen printed onto the tape using a paste containing fine metal particles dispersed in an organic vehicle. After drying the layers of tape are laminated together, pressed, cut and fired in air at temperatures in excess of 1300°C.

Unlike thick film conductor pastes the MLCC electrode materials contain only the metal and an organic vehicle system. The metals utilised for these high sintering temperature dielectric materials are restricted to palladium or a palladium rich palladium-silver alloy. Figure 6 shows a scanning electron micrograph of one such palladium powder used in this application. The powders, manufactured using sophisticated chemical routes, are produced to a very high level of purity and controlled morphology in order that they can be screen printed to the minimum possible thickness and will shrink on firing to form a coherent electrode structure at roughly the same rate as the dielectric which surrounds them. If any appreciable difference in the rate of shrinkage occurs then the MLCC will delaminate and must be discarded.

Considerable effort has been expended in a search for high permittivity dielectric materials which will sinter at lower temperatures and so allow the use of low melting point alloys containing higher levels of silver. A number of glass-ceramic materials have been discovered which fulfil this role and some are now being used commercially. While these new materials will undoubtedly supplant the use of high temperature systems in some applications, the performance advantages associated with the use of barium titanate/palladium will ensure their continued use.

The most common end termination materials for MLCCs are silver or silver rich palladium-silver alloys applied using a simple dipping operation and subsequently dried and fired using a tunnel furnace. The pastes used are very similar to fritted thick film palladium-silver inks except that different frit formulations are used to match to the ceramic body. Palladium-silver end terminations are generally preferred since, in common with conventional thick film materials, they can be fired in air to yield highly conductive layers which can be readily soldered without excessive silver removal by solder leaching.

The trend in MLCC manufacture has been to reduce costs by increasing automation, by thrifting palladium with silver wherever possible and by substitution of base metals. To date the only significant use of base metals has been for end terminations and this trend is likely to continue. While base metal buried electrodes for MLCCs are in existence none has had any appreciable impact on the market, and given the problems associated with their use this situation is unlikely to change in the immediate future.

**Summary and Outlook**

The platinum metals—long associated with the electrical industry—are now also well established in the microelectronics industry. Because of their unique physical and chemical properties, they are used to fulfil a wide range of the material requirements that are essential to the successful and continued development of microelectronic technology. This is of course supplemented by their ancillary applications involved in the manufacture of the basic microelectronic materials themselves.

Thick film technology accounts for the largest part of platinum metal consumption in the industry, particularly ruthenium for resistors and palladium for MLCCs. Although considerable effort has been expended to develop alternative materials, particularly base metal systems, the continued use of the platinum metals is assured in the near-to-medium-term and also in the long-term for high performance circuits. This is because technical problems associated with these competing systems still limit their use for many applications. Their use is particularly cost effective on the thin film side and a continued expansion of applications is expected, in sensing, display and IC technology itself. Microelectronics indeed represents a key area for growth and new technology for the platinum metals.
Improved Iridium Alloy Welds

FOUR-POLE OSCILLATION REDUCES HOT-SHORT CRACKING

The use of platinum group alloys to encapsulate radioactive heat sources in the thermoelectric generators that are used to provide electric power for instruments on unmanned spacecraft has been reported in this journal previously \(1, 2\). Heat released by the decay of an isotopic fuel, generally plutonium dioxide \(238\text{PuO}_2\), is converted into electrical power by its action on a collection of thermocouple elements. The plutonium dioxide must be safely contained under both normal operating conditions and those that could be encountered in the unlikely event of an aborted launch or later re-entry into the Earth's atmosphere.

Currently the radioactive pellets are encapsulated by welding together two 0.6mm thick iridium alloy cups. In addition to iridium, the alloy contains 0.3wt. per cent tungsten, 60±30ppm thorium and 50±30ppm aluminium, while welding is performed in a protective atmosphere of helium-25 per cent argon. Two-pole magnetic arc oscillation has been used to give the required grain structure. However, it is well known that iridium alloys suffer from hot-short cracking when the thorium concentration approaches rooppm, and in practice approximately one equatorial weld in five exhibits underbead cracking in the arc taper area. Ultrasonic inspection results in a seven per cent rejection rate, although in some batches of alloy this can rise to 26 per cent, an unacceptable level.

Now J. D. Scarbrough of E. I. du Pont's Savannah River Plant and C. E. Burgan of the Monsanto Research Corporation have reported that the frequency and severity of the weld cracking problem can be significantly reduced by the use of a four-pole magnetic arc oscillator (Welding J., 1984, 63, (6), 54–56). In their paper typical microstructures of the welds produced by the two methods are shown. Grain growth patterns are very similar but a 17 per cent reduction in grain size results from the use of the four-pole oscillator. Using given parameters, the overall production reject rate fell from 7 to 2 per cent, while batches of alloy that had previously suffered a 26 per cent rejection with the two-pole oscillator also had this rate reduced to 2 per cent when the four-pole oscillator was employed. Two primary causes are postulated for this improvement in the production reject rates.

The two authors suggest that the use of four-pole oscillation may also be beneficial when welding other alloys which are prone to hot-short cracking.

References

Rhodium-Iron Thermometers

Over the past ten years the platinum-sheathed rhodium-iron resistance thermometer (RIRT) has proved its reliability at temperatures between 0.5 and 20K. Now smaller, more rugged versions of the RIRT have become available. In one, designed for use up to 700°C as well as for cryogenic conditions, the resistance coil is mounted in an alumina and glass body. A recent report on the thermometric properties and stability of these ceramic RIRT’s by L. M. Besley of CSIRO, Division of Physics, Sydney (J. Phys. E: Sci. Instrum., 1984, **17**, (9), 778–781) concludes that despite small changes in resistance on handling the remarkable stability of these thermometers on thermal cycling together with their low self heating and reasonable sensitivity will make them useful for many low temperature applications.