

Monolithic Multilayer Ceramic Capacitors for Hybrid Circuits

THE EFFECTS OF TEMPERATURE CYCLING ON STABILITY

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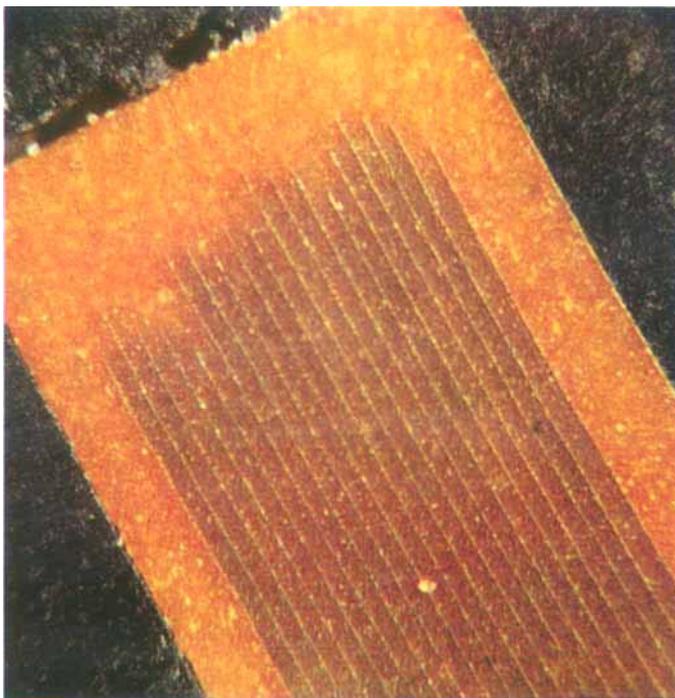
The development of miniature circuitry, and particularly of the hybrid film circuit, has demanded more and more capacitance in a smaller volume of capacitor. There are three possible ways in which this can be achieved. One is to produce capacitors without wires or encapsulation or any of the other appendages previously required by equipment designers. Another is to use thinner layers of dielectric, but this is limited by the voltage that the capacitor must withstand. The third is the use of higher dielectric constant materials, but unfortunately it is generally found that the higher the dielectric constant of a material the poorer is its stability.

This last point is illustrated by comparing the change in capacitance with temperature of two typical materials: one having a nominal dielectric constant of 1200 (known as K1200) will change its value of K

by as much as 20 per cent when its temperature is raised from -55°C (the lower limit stipulated by international specification) to room temperature, while a low dielectric constant ceramic having a K of, say, 30 – generally used for capacitors known as NPO for negative-positive-zero – will vary only by at most 0.25 per cent with the same change of temperature.

The monolithic multilayer ceramic capacitor is produced by screen printing on to strips of “green” ceramic of the barium titanate type an ink or paste incorporating finely divided platinum or a mixture of platinum group metals. A stack of these

The platinum metals not only provide the most reliable electrodes but also enable an economical production method to be employed in the manufacture of small monolithic capacitors. By screen printing and firing to form a robust integrated structure it is possible to obtain a very high ratio of capacitance to volume. This cross-section, magnified 50 times, shows the ceramic layers clearly separated by the platinum electrodes.



strips is then assembled and fired at about 1300°C to mature the substrate and fuse the layers into a block or chip. Metallising the ends of the chip with silver-palladium or gold-palladium then completes the contact between alternate electrodes. By this technique very thin dielectrics, which individually would be hopelessly fragile, may be used, while the fused structure is robust, hermetically sealed, and can be immediately incorporated into a hybrid circuit.

Ceramic substrates of many compositions can be used in monolithic chips, so that very high dielectric constants are available, but the stability of the capacitor clearly cannot be greater than that of the ceramic itself. The desire to use high K materials in the interests of miniaturisation can thus lead to difficulties because of the relatively poor stability of these materials. When subjected to high temperature processes such as soldering, for example, high K capacitors can show a drift in capacitance beyond acceptable limits.

Some recent work in the Electronics Laboratory of Matthey Printed Products was therefore designed to evaluate the change

in capacitance a monolithic chip capacitor is likely to undergo during the assembly and subsequent processing of a hybrid micro-circuit, and to provide the user with information that will allow him to anticipate this behaviour and make allowance for it. The detailed results of this work, reported at the recent Inter-Nepcon 70 Conference at Brighton, showed that, while the variations are predictable and repeatable and in some circumstances reversible, because of the diversity of techniques employed in the industry it would be unrealistic for a manufacturer of ceramic chips to specify a time by which a chip will recover its original capacitance after a soldering operation or any other heating cycle.

It was found, however, that the application of high voltages can accelerate the ageing and so stabilise the capacitance.

Further development along these lines should result in components having a limited temperature range in which they will operate satisfactorily, but having at the same time an unrivalled combination of stability and capacitance/volume ratio.

Zerovalent Complexes of Platinum

The discovery some twelve years ago of complexes in which platinum exhibits zero valency—that is, in which the platinum atom is associated only with uncharged ligands—has proved of considerable importance for the synthesis of a wide range of compounds, some of which might be of use in homogeneous catalysis. A typical example of such complexes is tetrakis(triphenylphosphine) platinum $[P(C_6H_5)_3]_4Pt$. In reactions involving this compound it has been postulated that the coordinatively unsaturated species $[P(C_6H_5)_3]_2Pt$ is a reactive intermediate. This means that there will be released in the reaction two triphenylphosphine groups which will still be available to compete for the vacant coordination sites. If the reactive intermediate could readily be prepared this situation would no longer exist, and the possibility would arise for even further advances to be made in the field of platinum organometallic chemistry.

In view of this, a paper by D. M. Blake and C. J. Nyman, of Washington State University, entitled "Photochemical Reactions of Oxalato-bis(triphenylphosphine)platinum(II) and Related Complexes" (*J. Am. Chem. Soc.*, 1970, 92, (18), 5359–5364) assumes significance. In an investigation of photochemical reactions of oxalato complexes a route to the co-ordinatively unsaturated compound has been discovered. Photolysis of an ethanol solution of $[P(C_6H_5)_3]_2C_2O_4Pt(II)$ under a nitrogen atmosphere, from which oxygen had been rigorously removed, resulted in the production of this complex in the form of a dimer, $[P(C_6H_5)_3]_4Pt_2$. Thus a relatively simple route to this reactive species has become available. Although only this one reaction has been noted here, others are described. It is apparent from this work that photolysis of oxalato complexes offers a route to reactive species for the production of catalytically active compounds in situ. F. M. L.