A THICK FILM BASE METAL RESISTOR AND COMPATIBLE HYBRID SYSTEM

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Non-noble metal thick film materials have been the topic of several recent papers.1,4,5 This paper will focus on the first non-noble metal thick film system comprising conductors, dielectrics and most important, resistors for commercial use. Processing and performance data are presented in detail to illustrate the capabilities of these new materials. Circuit applications information is presented wherever possible. This new class of materials will enable the microelectronics industry to exploit new market opportunities previously unavailable due to the high costs of precious metal materials.

1. INTRODUCTION

To assure the continued growth of the hybrid microelectronics industry, continued efforts to achieve lower manufacturing costs must be stressed. Obviously, direct material costs of a thick film circuit vary greatly, but it is a safe assumption that material cost is always a significant portion of the total circuit cost. The elimination of precious metal materials to achieve passive circuit functions is now a reality. Commercially available base metal compositions now offer the circuit manufacturer a viable alternative to noble metal thick films. The use of non-noble materials in the electronics industry is neither new nor unique.1-6

Several well known examples are the use of Copper plating depositions in the printed circuit board industry and the use of Tin Oxide, Indium Oxide7 and Thallium Oxide8-9 to manufacture resistive elements. Unfortunately, these earlier products were not marketed as a thick film system, but as individual materials.16 The development of a conventionally screen printed and fired base metal system is a new and viable concept. The necessary processing equipment such as atmosphere furnaces have been available for several years.10

Development of this system utilizes conventional methods of thick film material manufacturing in which finely divided particles of metals and glasses are dispersed in an organic medium. The materials are then processed into a screen printable paste form just as their noble metal counterparts. Some of the resultant base metal products exhibit performance characteristics equivalent to noble metal materials. Specific improvements have been made in the Copper conductor to permit routine printing of 4 mil lines with 4 mil spacings.11 This line resolution capability is equivalent to the state of the art in printing noble metal conductor materials.

This paper will define the characteristics, capabilities, and economics of a base metals approach to thick film technology. Each part of the system, i.e., resistors, conductors, and dielectrics will be examined and defined. Specific circuit applications, as well as potential applications utilizing this base metal system will be discussed.

2. THE NPS BASE METALS SYSTEM

The NPS base metals system comprises the following materials:

<table>
<thead>
<tr>
<th>A. NPS Resistors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Part no.</td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>7150</td>
</tr>
<tr>
<td>7200</td>
</tr>
<tr>
<td>7300</td>
</tr>
<tr>
<td>7400</td>
</tr>
<tr>
<td>7500</td>
</tr>
</tbody>
</table>
B. NPS Conductors

<table>
<thead>
<tr>
<th>Part no.</th>
<th>Resistivity (ohms/sq., microns-thick)</th>
<th>Metallurgy</th>
<th>Viscosity (poise)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7028</td>
<td>0.060 at 20</td>
<td>Nickel</td>
<td>3000</td>
</tr>
<tr>
<td>7029d</td>
<td>0.003 at 18</td>
<td>Copper</td>
<td>4000</td>
</tr>
</tbody>
</table>

C. NPS Dielectrics

<table>
<thead>
<tr>
<th>Part no.</th>
<th>Dielectric constant a (K)</th>
<th>DF a</th>
<th>IR (ohms)</th>
<th>TCC b (poise)</th>
<th>Viscosity (poise)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7115</td>
<td>9–10</td>
<td>0.005</td>
<td>10^{13}</td>
<td>+350</td>
<td>2000</td>
</tr>
<tr>
<td>7115B</td>
<td>7.5–8.5</td>
<td>0.010</td>
<td>10^{12}</td>
<td>+700</td>
<td>2000</td>
</tr>
</tbody>
</table>

a Measured at 1 kHz.

b *25°C to +85°C.

The many processing similarities between the NPS systems and the more familiar noble metal systems will not be discussed. Instead, important differences and the dissimilarities will be presented in some detail.

Fortunately, the systems differ in only two areas: namely, the drying process and the firing process.

The processing of finely divided base metal particles at elevated temperatures requires additional precautions not required with precious metals. For example, consider the following reactions in air at about 500°C for 5 micron powders:

\[
\begin{align*}
\text{Cu}^0 + \frac{1}{2} \text{O}_2 \text{ (air)} & \rightarrow \text{CuO} \\
\Delta H_0 &= -37740 \text{ gm cal. mole}^{-1} \quad (1) \\
\text{Au}^0 + \text{O}_2 \text{ (air)} & \rightarrow \text{AuO} \\
\end{align*}
\]

One can readily see that in Eq. (1) Copper Oxide will be formed quite easily as evidenced by the very large negative heat of formation \((\Delta H_0)\). Gold metal remains unchanged and will not form stable oxides at these temperatures.

This information is presented to demonstrate that base metals are prone to oxidation when exposed to excessive temperatures during processing. Actual experience has shown that if one establishes a reproducible, precise drying schedule for processing these base metal thick films, results will be consistent. Inconsistent drying operations produce variations in oxide films and yield unsatisfactory results. A recommended drying sequence is **150°C for 5 minutes** when drying resistor and conductor materials. A 10 minute drying time at the same temperature is recommended when processing dielectric materials.

After drying, firing in a Nitrogen atmosphere is necessary to prevent oxidation of the dried films. Optimum firing conditions are 900°C for 6 minutes dwell for all NPS materials. Permissible processing range is 875°C–925°C over a dwell time of 6–8 minutes. Many furnace manufacturers produce equipment capable of maintaining the desired Nitrogen cover. An earlier paper \(^{10}\) has shown that the cost of providing Nitrogen cover gas in the furnace to be about $0.90/hr. at gas flow rates of 150 SCF/hr. (4.85 m³ hr⁻¹). These flow rates will adequately process at least 500 - 1 x 2 inch substrates per hour.

A qualitative comparison between conventional air injected furnaces and Nitrogen furnaces suggests approximate cost equality when one considers cost of compressor operation, air dryers, filters, etc. In addition, the cost of Nitrogen gas is negligible when compared with the thick film material savings that can be realized.

A chronological development is presented in the figure below.
Figure 1 illustrates the chronological development of commercially available thick film materials. Significant resistor production using base metal or refractory metal materials has been achieved for many years by various companies using proprietary base metal materials. This point is made to demonstrate the feasibility of this approach.

Figure 2 illustrates the relative material cost of the base metal system and the more widely used noble metals. For comparison purposes, approximate cost at a 3 kilogram purchased material level is presented. As acceptance of these materials occur in the market place and production economies are realized, resistor materials should sell for less than $10.00 per ounce, and conductors should sell for less than currently available silver conductors.

A number of applications areas have been identified for NPS materials. These will be amplified in the last section of this paper. Microwave strip line circuits multilayer interconnection circuitry, capacitor terminations, and D.C. gas display panels are current applications areas for existing materials. Near term opportunities for base metal products include telecommunication circuits, low cost resistor-conductor networks, and metallization of porcelainized steel substrates.

3. SYSTEM COMPONENTS

3.1 NPS Resistor

3.1.1 General The availability of a resistor system that is compatible with Copper and Nickel metallizations is an important step in achieving a truly low cost thick film paste system. The Cermalloy NPS resistor system consists of a finely divided glass, with Tantalum metal, plus other base metal oxides for TCR and resistivity control.

![Figure 3](image)

**FIGURE 3** Sheet resistance vs. weight percent of conductive phase.

![Figure 4](image)

**FIGURE 4** Sheet resistance vs. temperature coefficient of resistance.

![Figure 5](image)

**FIGURE 5** Sheet resistance vs. peak firing temperature.
0.5% per °C change in peak firing temperature over firing temperatures from 870°C to 925°C. This change is comparable to air firing Ruthenium Oxide materials.

Figure 6 illustrates the effect of dwell time at peak firing temperature on sheet resistivity. Variation of dwell time for the 100 and 1000 ohm materials causes negligible changes in resistivity. However, the resistivity of 10 kohm material decreases as the time at peak temperature increases.

3.1.2 Resistor stability The following data illustrate resistor system stability under various stress situations. Test data accumulated to date suggests a drift rate of less than 0.5% after 1000 hour exposure to ambient of 150°C. This is presented graphically in Figure 7, showing individual resistivity ranges tested.

Load life testing at 100 watts/sq.in. for 100 hours at 70°C is presented in Figure 8. Resistance changes here are less than 2%. Humidity testing when passivated with a Cermaloy 5200 epoxy cover coat minimizes resistivity changes. Less than 1% change in 1000 hours of exposure to a 95% relative humidity environment, is a typical performance when properly passivated.

Exposure to humidity or moisture will produce undesirable resistance changes if the resistor surface is not properly passivated. The effect of solder exposure on NPS resistors is typically a 0.1% change after 10 second immersion in 60Sn40Pb solder at 250°C.

The current noise characteristics are presented in Figure 9. This data shows the NPS resistors have a higher noise level than presently used Ruthenium Oxide resistors. This difference is undoubtedly due to the particle size and shape of the NPS resistors relative to the more highly developed Ruthenium Oxide materials with smaller particle size. Future work with smaller particulate NPS materials may improve the noise characteristics of this system.

3.1.3 Trimming characteristics Abrasive trimming can be accomplished in the same manner as other thick film materials, using standard techniques.

Limited experience with laser trimming indicates that a higher than conventional power level is necessary to satisfactorily remove the more refractory materials contained in NPS resistors.
A Union Carbide Corp. Model No. KRT Q switching type laser trimmer was used to provide a simple plunge cut configuration. As-fired resistor values were noted and a 20% trim resistance adjustment was made. This percentage of trim provides a trim configuration adequate to show variation in resistor performance due to trimming.

The laser trimming parameters selected are as follows:

- Peak Power: 1.8 kW
- Repetition Rate: 260 Hz
- Linear Trim Rate: 50 Mils/sec.
- Laser Cut Type: Single plunge

The following tabulation summarizes the data. Notice that both the 100 hours room temperature drift, as well as 500 hour - 150°C drift are less than 0.25%.

<table>
<thead>
<tr>
<th>Initial R value (ohms)</th>
<th>20% trimmed R value (ohms)</th>
<th>100 hour avg. drift-%</th>
<th>500 hour avg. drift-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>125</td>
<td>150</td>
<td>±0.1</td>
<td>0.23</td>
</tr>
<tr>
<td>1.4K</td>
<td>1.7K</td>
<td>±0.1</td>
<td>0.08</td>
</tr>
<tr>
<td>8.4K</td>
<td>10.0K</td>
<td>±0.2</td>
<td>0.06</td>
</tr>
</tbody>
</table>

3.2 Conductors

3.2.1 Copper conductor 7029 The specific properties of the Copper conductor, Cermalloy 7029 have been elucidated in recent papers by Grier and Wood and hence will be presented here only in summary form. For greater detail, it is suggested that these references be consulted.

A Copper thick film conductor material can be a truly high performance, low cost product. The conductivity of 7029 Copper is 3.2 milliohms per square at 15 microns fired thickness and is comparable to thick film Gold conductors. Figure 10 contrasts the resistivity of several thick film metallizations available in the market. This exceptionally high conductivity value of 7029 Copper has permitted its use in circuits from DC to at least 8 GHz at a great cost savings over thin film Chrome/Gold and high density thick film Gold stripline approaches.

Figure 11 shows the actual difference in microwave insertion loss between 7029 Copper and a commercial thick film Gold, over the frequency of 1 to 8 GHz.

Figure 12 shows fine line capability of Copper on an Alumina substrate. Line widths as small as 4 mils (100 microns) are easily resolved.

In addition to being a highly conductive material, the 7029 Copper also wire bonds over reasonably broad processing parameters. Figures 13 and 14 show initial and aged wire bond strengths in grams for 1 mil Aluminum wire. Note that the loss of adhesion due to ageing at 155°C for 168 hours is negligible.
Similar results are obtained on soldered adhesion peel tests using 100 mil\(^2\) (2.5 mm\(^2\)) pads and a 60Sn40Pb solder composition. Figure 15 typifies results of a 2000 hour 150\(^\circ\)C solder ageing test revealing negligible loss of adhesion. This feature of the Copper suggests possible use for high reliability applications where soldered circuitry is exposed to high ambient operating temperatures. The adhesion retention after prolonged high temperature exposure is an outstanding advantage of this material, which should be exploited.

Wood\(^9\) has evaluated various plating techniques for compatibility with Copper thick film and found electroplating Gold to be acceptable, while electroless Gold and Tin plating processes attacked the Copper and caused adhesion degradation.

3.2.2 Nickel conductor 7028 The thick film Nickel conductors are widely used as electrode material for D.C. gas discharge display panels. This conductor is normally fired onto soda-lime glass substrates at temperatures not exceeding 600\(^\circ\)C for display panel applications.

As a termination material for NPS resistors, it is capable of being fired at 900\(^\circ\)–950\(^\circ\)C. Nickel conductors are typically more difficult to solder, less adherent to the substrate and considerably less conductive than Copper materials and hence have found limited applications.

3.3 Dielectrics

The development of Nitrogen firing dielectric pastes
permits the manufacture of complex multilayer circuitry for interconnection applications. Cermalloy dielectric compositions 7115 and 7115B have been designed to be compatible with Copper 7029 while closely matching the expansion characteristics of a 96% Aluminum Oxide substrate to minimize substrate distortion problems. The electrical properties of these materials were summarized in Section 2 of this paper. The proper processing of dielectric materials is of prime importance if high circuit yields are expected.

The printing and drying processes should occur in a clean, dust free environment. The following processing conditions are recommended to obtain high yield multilayer circuits using either 7115 or 7115B dielectric materials:

1) Clean substrates prior to printing dielectric material.
2) Print 2 wet passes per dielectric layer.
3) Dry at 150°C for 10 minutes.
4) Fire at 900°C for 7 minutes dwell in 150 SCFH flowing Nitrogen gas.

5) Repeat steps 2, 3 and 4.

6) Total fired deposition thickness to be 40–50 microns.

Experience has indicated that a separate firing of Copper conductor on top of the dielectric is preferred to cofiring to eliminate or minimize materials interactions. Cofiring generally contributes excessive material reactions and reduces product yields.

A 12–15 mil via resolution capability is characteristic of these dielectric materials. Very large substrate sizes, for example 4 in. x 4 in., appear to limit resolution of vias to 15 mils.

Figure 16 illustrates a simple 2 metallization layer multilayer test circuit utilizing 7115B dielectric and 7029 Copper materials. This circuit has been processed in accordance with the above instructions. Figure 17 shows greater detail of the completed circuit, using 7115 dielectric. The Copper conductor lines in the upper right are 100 microns wide. These particular circuit materials constitute the basic multilayer capability of this system. The 7115B is a denser, lower K dielectric material than 7115 and it fires to a permanent blue colour. The 7115B also permits easier solderability of Copper on top of the dielectric. The adhesion strength of the soldered Copper on top of 7115B is superior to that on top of 7115. We suspect these differences are due to the greater film density and opacity of the 7115B.

Actual production experience using either dielectric with the 7029 Copper conductor has demonstrated that multilayer circuitry can be manufactured at high yields using base metal conductors.

4. SYSTEM APPLICATIONS

Previously, several application areas were identified as being suitable for, and compatible with the NPS system characteristics. These include microstrip circuitry up to at least 8 GHz, high density interconnections, resistor-conductor networks, high power diode metallization, terminations for capacitors, D.C. gas display panels, solar cell metallization materials, metallization for enamelled stainless steel substrates, and metallization for Beryllia ceramics.

The primary advantages of a Nitrogen processable resistor system are that it provides for the use of inexpensive Copper and Nickel conductors and that, it is itself a low cost system. This becomes apparent when one considers that the conductor material usually constitutes the largest material cost in the circuit.

Figure 18 shows a typical stripline circuit configuration having some moderate area printing, and conductor traces 25 and 10 mils (0.62 and 0.25 mm) in width. The conductor traces should be uniform to ±1 mil (±25 microns) in width. The fired conductor film density should be high with a fired thickness of from 0.7 to 1.0 mils (18 to 25 microns). As shown earlier, the Copper is comparable in performance to thick film Gold and thin film Chrome-Gold for most microstrip circuits up to the low GHz frequencies. Furthermore, the use of Copper eliminates the necessity of expensive Indium bearing solders and permits the use of common Tin-Lead solders. The NPS resistors are ideally suited for such high frequency circuits since the performance characteristics of the desired lower resistance range (10 ohms to 1000 ohms) are competitive to the presently used air fired
systems. Thus, screen printing of NPS resistors directly onto the Copper microstrip circuits is feasible.

A wide variety of characteristics are monitored during the fabrication of circuits; of greatest concern are: maintaining high conductivity with thin conductor traces, solderability and adhesion of top conductors, and good dielectric via control. This system provides thin conductor traces of better than 3 milliohms per square with dielectric-conductor adhesion strengths typically over 8 pounds peel on a 100 mil² (2.5 mm²) peel test. The dielectric material is glassy and therefore has a high cohesive film strength necessary for over printing metallizations.

Copper thick film is compatible with certain capacitor compositions of the non-reduced Titanate.
variety. Ultimately, the Copper paste used would be cost competitive with presently used Silver metallizations. In addition to the cost advantage, Copper would considerably suppress problems arising from characteristic metal price fluctuations.

The Copper metallized circuit shown in Figure 19 provides for flip chip reflow solder attachment of a four bump integrated circuit chip. A reflow solder attached package cap may be employed as a means of protecting the chip here.

Figure 20 shows two examples of high power circuit metallizations. The large substrate shown in the upper part of the picture is 96% Alumina with high adhesion Copper. The disc is Beryllia using the same Copper metallization material. Each circuit accommodates a reflow solder attached high power chip. The metallization used for reflow solder attachment of high power integrated circuit chips such as SCR's is usually plated Moly-Manganese. A single print of Copper will provide such a circuit with the additional advantage of an efficient thermally conductive metallization. The Copper is a mix-bonded formulation, providing little resistance to heat dissipation.

The small parts (0.75 x 0.13 inches) shown in Figure 21 are printed with base metal resistors terminated to Copper or Nickel conductors. This configuration is used in trigger switches for variable speed drill and saw motors.

Large quantities of thick film Nickel and black dielectric are presently being used in the manufacture of D.C. panels. Nickel is fairly non-reactive to Mercury, which is present in D.C. gas panels. This is an advantage as well as the low cost and low processing temperature on soda-lime glass. Other volume applications are displays for point-of-sale computer cash registers and CRT games. These materials are processed on plate glass at about 600°C. A variety of
multiplexing circuit configurations are employed, using the multilayer capability.

Figure 22 shows both 2 and 3 inch diameter Silicon solar cells having Copper thick film electrodes. The “sun-side” of such a cell typically has a shallow diffusion layer to maximise cell efficiency. Because of this, the conductor material required for electroding must be compatible with the lower temperature processing conditions and with the Silicon system to protect the junction characteristics. Present uses of panels and cells include power supply to remote electronic instruments, construction bridge structure, biasing to prevent galvanic degradation and (arid region) water pumping power units. If other problems relating to cost and efficiency can be solved, a very large potential for electronic materials may evolve.

The technological area which lies between P.C. board circuits and hybrid thick film circuits may be described as requiring the large area of a P.C. board and the high temperature and flexural stability of a ceramic circuit. Porcelanized steel substrates using base metal conductors may well fill this technological gap. Fabrication of these circuits combine the advantages of low temperature processing ($<600\,^\circ C$ peak temperature), low cost substrates, low cost base metal conductors, selective metal deposition, solderability, through-hole printing and long term thermal and mechanical stability.

5. CONCLUSION

A compatible base metal thick film hybrid materials system is presented in this paper. It comprises Nickel and Copper conductors, dielectric for multilayer and low capacitance and a base metal resistor paste. Particular emphasis is placed on the resistor characteristics in as much as it is the newest and probably the most sophisticated member of the system. Although substantial refinements in further paste development and processing conditions are indicated, it is believed that this hybrid system, in its present form, represents a useable and dependable new approach to the manufacture of hybrid circuitry today.

Base metal pastes are no longer considered a novelty. Nickel and Copper conductors have been used successfully in product manufacturing for over two years. It is reasonable to project not only a significant increase in cost effectiveness with the use of these materials, but certain technical advantages which are shown in this paper will widen the range of opportunities for thick film technology.

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