Lead-free low-firing thick-film resistors based on bismuth glasses and ruthenium oxide

Thomas MAEDER, Caroline JACQ, Claudio GRIMALDI and Peter RYSER

Laboratoire de Production Microtechnique, École Polytechnique Fédérale de Lausanne (EPFL-LPM) 
CH-1015 Lausanne, Switzerland, http://lpm.epfl.ch.

Abstract: Recent developments in thick-film technology have seen the widespread introduction of lead-free alternative to traditional conductive, dielectric and overglaze compositions. Resistors, however, have lagged behind this trend, as developing balanced and well-behaved resistive compositions from scratch is significantly more involved than other thick-film materials. Bismuth-containing glasses based on the bismuth-zinc-boron-silicon oxide system, which have been studied for over 20 years, constitute a promising alternative to the usual lead borosilicate materials, with which they are quite similar. This paper presents, after a historical perspective of thick-film resistor technologies, a short overview of bismuth glasses and recent developments in applying them to lead-free thick-film resistors, with a focus on low-firing piezoresistive compositions. Recent work, both outside and in our laboratory, suggests that successful development of these novel lead-free materials is possible, and that they can be applied to the manufacture of thick-film piezoresistive sensors on steel substrates. Moreover, as firing temperature below 600°C are achievable, application on glass and some aluminium alloys is also possible.

Key words: thick-film electronics, resistors, lead-free, bismuth-bearing glass frits, piezoresistive sensors.

1. THICK-FILM RESISTORS

1.1. Thick-film technology & sensors

Thick-film technology is an excellent platform for high-reliability electronics and packaging in applications such as automotive and aerospace, due to its excellent stability [1-7]. More recently, these outstanding properties has led to it being also applied to sensors [8-9], and extensions such as low-temperature cofired ceramic (LTCC), which features extended 3D structuration capabilities, have expanded the field even wider, to novel devices possibly combining sensor, actuators and fluidics circuits [10-12].

1.2. Chemistry of standard thick-film resistors

Thick-film circuits on ceramic substrates initially served only as carriers, much like organic printed circuit boards (PCBs), and the introduction of compositions for thick-film resistors (TFRs) represented a major advance. However, first-generation resistive compositions, based on the Ag / PdO in a lead borosilicate glass matrix [4,13] suffered from considerable process sensitivity. These problems were considerably alleviated when TFRs based on fine dispersions of RuO$_2$ conductive particles in a lead borosilicate glass frit were introduced towards the end of the 1960s [14]. Modern TFRs are refined versions of this system, where RuO$_2$ may be replaced by similar IrO$_2$ (both feature rutile structure and metallic conductivity [15]) and/or be incorporated into more complex phases [4], allowing fine-tuning of the properties. These complex oxides have the pyrochlore or perovskite structure and may incorporate Ru or Ir (i.e. ruthenates / iridates) [16-22]. Detailed investigation of commercial TFR series [20-23] showed the use of rutile RuO$_2$, pyrochlore Pb$_5$Ru$_2$O$_{6.5}$ or pyrochlore Bi$_2$Ru$_2$O$_7$ as the conductive phase, and confirmed the glass frit was based on lead borosilicate, which gives an overall volume makeup schematised in figure 1.
This resistor chemistry suggests possible particle-glass chemical reactions, as Bi$_2$O$_3$ and PbO may be both in the glass and in the particles, and the configuration before firing may not be the equilibrium one. This is common in commercial systems, which frequently combine Bi$_2$Ru$_2$O$_7$ as the (initial) conductive phase dispersed in lead borosilicate glass, giving rise to exchange of Bi$_2$O$_3$ and PbO between the glass and the conducting phase [20-22]. One may write the following main chemical equilibria:

\[
\begin{align*}
2(\text{BiO}_{1.5}\text{, PbO})[g] + 2\text{RuO}_2[r] & \leftrightarrow (\text{Bi, Pb})_2\text{Ru}_2\text{O}_{6...7}[p] \\
\text{BiO}_{1.5}[p] + \text{PbO}[g] & \leftrightarrow \text{BiO}_{1.5}[g] + \text{PbO}[p] \\
\text{RuO}_2[r] & \leftrightarrow \text{RuO}_2[g] \\
(\text{Bi, Pb})_2\text{Ru}_2\text{O}_{6...7}[p] & \leftrightarrow 2(\text{BiO}_{1.5}, \text{PbO})[g] + 2\text{RuO}_2[g]
\end{align*}
\]

where:

| g | glass phase |
| r | conductive particles: rutile RuO$_2$ (or IrO$_2$) phase |
| p | conductive particles: pyrochlore ruthenate (or iridate) phase |

Equation (1) relates to the equilibrium between the pyrochlore ruthenate phase and the simple rutile oxide, and (2) describes the equilibrium composition of the pyrochlore phase relative to that of the glass. (3) and (4) relate to dissolution into / precipitation from the glass, which are quantitatively small (but may play an important role in the electrical properties!) due to the low solubility of RuO$_2$ in the glass [24]. Note that stoichiometry is assessed on a cation basis in this work, e.g. Bi$_2$O$_3$ is written as "BiO$_{1.5}$", better reflecting its interchangeability with PbO. Reactions of type (1) and (2) have indeed been observed experimentally [21-23], and a detailed study, for PbO only, established lead ruthenate was stable / formed only at moderate temperatures in glasses with lead concentrations much higher than that used in commercial systems [25]. This was confirmed in our studies on model RuO$_2$-glass TFRs [26,27]. Therefore, most ruthenate-based formulations are not at thermodynamical equilibrium during firing. However, even in model systems where the conducting phase is thermodynamically stable (in practice, those formulated using RuO$_2$), the glass composition strongly influences the resistivity [26-28].

It must be additionally noted that the oxygen stoichiometry of Pb$_2$Ru$_2$O$_{6...7}$ is somewhat uncertain. Previous work [19] set it at 6.5, a value obtained by thermogravimetry and subsequently confirmed by neutron diffraction [29] that implies an average valence of +2.5 for Pb (or +4.5 for Ru?) in this compound. This adds a further complication, as formation / decomposition of lead ruthenate may involve a change of the oxidation state of Pb, requiring exchange of oxygen with the firing atmosphere. The occurrence of such phenomena is supported by results of TFR annealing studies in different atmospheres [30].

Besides the conducting filler and glass phase, in order to tune and control the resistivity and temperature coefficient of resistance (TCR), commercial resistor compositions contain oxide additives whose role has been extensively studied [31]. Selected additives also allow reliable fabrication of high-value resistors [32].
1.3. Electrical transport and piezoresistivity in TFRs – model systems

Given their microstructure [20-23], TFRs belong to the class of percolating materials, and their electrical conduction properties are therefore related to a wide range of percolation phenomena [33]. Compared to dispersions of metallic powders in continuous insulators, TFR compositions exhibit (1) an unusually low percolation threshold and (2) a much more progressive transition from insulating to conducting behaviour as the volume fraction of the conducting phase is increased [20, 34], which allows a good control of their characteristics. Such remarkable properties stem from (1) a "segregated" microstructure [34], as depicted in figure 2, and (2) an interparticle conduction process not dominated by direct contact, but by transport through a thin insulating layer - which has been shown to exist [35] - between adjacent conducting particles.

Figure 2. Microstructure and conduction mechanism of thick-film resistors (redrawn from [27]).

Much theoretical and experimental work, including from our group, has been devoted to the elucidation of the conduction mechanism, especially near the percolation threshold [20,34,36-42]. Most evidence suggests interparticle transport at ambient temperatures is dominated by tunnelling processes, which also determine the relatively high piezoresistive properties of these materials (see [43] for the relation between piezoresistivity and the more common "gauge factors"). Besides their technological importance, the piezoresistive behaviour of TFR sheds considerable light on their transport properties [40].

1.4. Application to piezoresistive sensing on metal substrates – low-firing systems

Piezoresistive sensors for pressure and force based on the favourable piezoresistive properties of TFRs (deposited on ceramic substrates) have found widespread use. However, in pressure sensors, the commercially most important application, standard thick-film technology faces important drawbacks

- Ceramics are brittle, and alumina has only mediocre mechanical properties, posing a significant bursting hazard upon overload. Additionally, the required polymeric seals / gaskets are often unacceptable in the chemical, food processing and refrigeration industries. Finally, the mechanical fixtures required to tighten the ceramic sensing element onto the sensor body ultimately limit the achievable precision.

- Using a weldable metallic sensing element solves all these problems, but the harsh standard firing conditions (850°C 10 min) alter the metallurgy of the alloys. In the case of steels, this does not allow application of high-strength martensitic types (see detailed discussion below). Titanium alloys have been successfully explored [44], but are much more expensive and require protection from oxidation. Therefore, thick-film sensors on metal substrates commonly apply standard ferritic [45] and austenitic [46] stainless steel grades, whose poor mechanical properties are exacerbated by the annealing effect caused by the harsh thick-film firing schedule.

Therefore, thin-film (semiconductor or metal gauge) on steel is the currently standard technology for high-accuracy, high-pressure industrial piezoresistive pressure sensors [47]. The moderate processing temperatures permitted by thin-film deposition is very favourable, as it allows the use of alloys combining very high strength and moderate cost, such as the precipitation-hardened martensitic (maraging) stainless steels [48]. However, thin-film deposition, especially of the dielectric layer, is time-consuming and involves expensive equipment. Therefore, a lower thick-film process temperature, compatible with high-strength steels, would allow low-cost manufacture of high-performance industrial pressure sensors.

Common maraging steels start to transform to the austenitic phase above ca. 700-750°C [49]; the subsequent martensitic transformation upon cooling and associated volume expansion will cause destruction by widespread cracking of an overlying thick-film circuit. In practice, process temperatures up to ca.625°C are acceptable [50]. Alternatively, austenitic precipitation-hardenable steels such as A286 [51], somewhat less common and lower-strength, are compatible with higher processing temperatures, up to almost 750°C. Special steels compatible with the standard thick-film process exist [52], but they are very expensive.
Recently, we have successfully applied such low-firing thick-film material systems on high-strength steels to pressure sensors [52]. In these systems, both dielectrics and resistors were based on filled lead borosilicate glasses, with the conductive phase in the resistors being RuO$_2$ and the firing temperature lowered by using high-lead glasses (75% PbO by mass). The attendant increase of the coefficient of thermal expansion (CTE) is not a problem here; it actually lowers the mismatch with steel.

2. BISMUTH GLASSES

2.1. From lead to bismuth glasses

Besides acting as a matrix in resistors, glass frits are widely used in thick-film electronics [1-4], as binders, adhesion promoters, sealing glasses, etc. Traditionally, most low-melting frits were based on the lead (zinc) (boro)silicate system. However, the European RoHS directive [53] puts pressure on the industry to remove lead, although PbO is still currently allowed in electronic glasses as an exemption. Although lead-free dielectric, conductor and overglazes are now commercially available, resistors have lagged behind in this trend, mainly due to their complex chemistry and physics. In this light, glasses based on Bi$_2$O$_3$ appear the most promising "drop-in" replacement for PbO-based ones, i.e. the one requiring the least development effort. The similarity of Bi$_2$O$_3$ and PbO was noticed in several studies [54-57]; like PbO, Bi$_2$O$_3$ belongs to the class of "conditional glass formers": while it does not by itself readily form a glass, it can be incorporated in very large quantities in the glass forming oxides SiO$_2$, B$_2$O$_3$ and P$_2$O$_5$, where it acts as a glass modifier at low concentrations, but as a glass former at higher ones. Given this similarity and in light of the aforementioned reactions occurring between lead borosilicate glasses and bismuth ruthenate fillers, it would seem logical to use a Bi-based glass in order to enhance resistor stability to firing. This would also lessen the property changes that classical resistors formulated with Pb-based frits encounter when fired with Bi-containing terminations [58].

Many bismuth-based glasses have been investigated, but "practical" glasses seem essentially based on the quaternary Bi$_2$O$_3$-ZnO-B$_2$O$_3$-SiO$_2$ system, with Al$_2$O$_3$ added in most cases. A set of similar low-melting bismuth- and lead-based glasses is listed in Table 1, together with their CTE and softening temperature $T_w$ (glass Bi12: very rough estimate). As for lead-based glasses, $T_w$ decreases and CTE increases when Bi$_2$O$_3$ is added, whereas the opposite effect is obtained with an increase of SiO$_2$ and/or Al$_2$O$_3$. However, ZnO and B$_2$O$_3$ do not follow this trend: increasing ZnO at the expense of B$_2$O$_3$ tends to somewhat lower both $T_w$ and CTE (see [59] 02-04).

Table 1. Comparison of low-melting bismuth- and lead-based glasses. Compositions on a cation molar basis.

<table>
<thead>
<tr>
<th>Ref/No</th>
<th>PbO [mol%]</th>
<th>BiO$_{1.5}$ [mol%]</th>
<th>ZnO [mol%]</th>
<th>BO$_{1.5}$ [mol %]</th>
<th>SiO$_2$ [mol %]</th>
<th>AlO$_{1.5}$ [mol %]</th>
<th>Other [mol %]</th>
<th>$T_w$ [°C]</th>
<th>CTE [ppm/K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[27] V2</td>
<td>22.8</td>
<td>57.9</td>
<td>16.1</td>
<td>3.2</td>
<td></td>
<td></td>
<td></td>
<td>500</td>
<td>7.0</td>
</tr>
<tr>
<td>[27] V6</td>
<td>36.8</td>
<td>31.5</td>
<td>27.4</td>
<td>4.3</td>
<td></td>
<td></td>
<td></td>
<td>450</td>
<td>9.0</td>
</tr>
<tr>
<td>[27] V8</td>
<td>48.2</td>
<td>36.3</td>
<td>10.5</td>
<td>5.0</td>
<td></td>
<td></td>
<td></td>
<td>380</td>
<td>10.5</td>
</tr>
<tr>
<td>[60] 20</td>
<td>41.3</td>
<td>11.4</td>
<td>41.5</td>
<td>5.8</td>
<td></td>
<td></td>
<td></td>
<td>380</td>
<td>10</td>
</tr>
<tr>
<td>[60] 18</td>
<td>57.2</td>
<td>9.0</td>
<td>33.7</td>
<td>5.3</td>
<td></td>
<td></td>
<td></td>
<td>330</td>
<td>12</td>
</tr>
<tr>
<td>[61] 01</td>
<td>44.1</td>
<td>11.8</td>
<td>38.7</td>
<td>5.3</td>
<td></td>
<td></td>
<td></td>
<td>450</td>
<td>8.9</td>
</tr>
<tr>
<td>[61] 02</td>
<td>51.8</td>
<td>16.4</td>
<td>19.2</td>
<td>12.6</td>
<td></td>
<td></td>
<td></td>
<td>450</td>
<td>8.3</td>
</tr>
<tr>
<td>[61] 03</td>
<td>54.0</td>
<td>2.7</td>
<td>23.8</td>
<td>19.5</td>
<td></td>
<td></td>
<td></td>
<td>480</td>
<td>8.4</td>
</tr>
<tr>
<td>[59] 01</td>
<td>30.0</td>
<td>19.0</td>
<td>39.0</td>
<td>12.0</td>
<td></td>
<td></td>
<td></td>
<td>550</td>
<td>7.5</td>
</tr>
<tr>
<td>[59] 02</td>
<td>40.0</td>
<td>15.0</td>
<td>35.1</td>
<td>9.9</td>
<td></td>
<td></td>
<td></td>
<td>525</td>
<td>9.4</td>
</tr>
<tr>
<td>[59] 03</td>
<td>44.0</td>
<td>18.8</td>
<td>26.4</td>
<td>9.1</td>
<td>1.6</td>
<td></td>
<td></td>
<td>500</td>
<td>9.3</td>
</tr>
<tr>
<td>[59] 04</td>
<td>40.0</td>
<td>30.0</td>
<td>19.9</td>
<td>7.6</td>
<td>2.6</td>
<td></td>
<td></td>
<td>495</td>
<td>8.5</td>
</tr>
<tr>
<td>[59] 30</td>
<td>42.1</td>
<td>13.6</td>
<td>25.0</td>
<td>6.0</td>
<td>2.4</td>
<td>10.0 BaO</td>
<td>0.9 NaO$_{1.5}$</td>
<td>470</td>
<td>10.6</td>
</tr>
<tr>
<td>[59] 34</td>
<td>41.3</td>
<td>15.3</td>
<td>32.2</td>
<td>6.2</td>
<td>2.4</td>
<td>2.4 BaO</td>
<td></td>
<td>440</td>
<td>9.6</td>
</tr>
<tr>
<td>[59] 35</td>
<td>48.6</td>
<td>0.8</td>
<td>11.8</td>
<td>37.5</td>
<td>1.3</td>
<td></td>
<td>1.5 CaO</td>
<td>0.1 MgO</td>
<td>0.1 CuO</td>
</tr>
<tr>
<td>[62]</td>
<td>33.3</td>
<td>19.1</td>
<td>-</td>
<td>45.7</td>
<td>0.2</td>
<td></td>
<td></td>
<td>480</td>
<td>10.4</td>
</tr>
<tr>
<td>[63] Bi12</td>
<td>40.0</td>
<td>15.0</td>
<td>35.0</td>
<td>6.0</td>
<td>4.0</td>
<td></td>
<td></td>
<td>(430)</td>
<td></td>
</tr>
</tbody>
</table>
Given the above considerations, it is expected that a plot of $T_w$ vs. $CTE$ (figure 3) will give considerable scatter, a problem exacerbated by the lack of directly comparable data. Overall, the Bi$_2$O$_3$-based glasses in this system reach $T_w$ values roughly 50–80 K above that of PbO ones, which is still acceptable; this corresponds to the V6 glass in our previous studies, which allows fabrication of resistors suitable for firing around 600°C [40], yet still having – in contrast to even lower-firing V8-based TFRs - good stability [26].

![Figure 3. Plot of data in table 1 (softening temperature vs. th. expansion), for bismuth- and lead-based glasses.](image)

2.2. Resistors using bismuth-based glasses

Recently, first results have been published on lead-free TFRs with bismuth-based glasses and RuO$_2$ conducting particles [62-64]. While the first work [62] used a relatively high-melting glass (low Bi$_2$O$_3$ and high SiO$_2$) and standard firing temperatures around 850°C, the work by our group [63] (see table 1) and another [64] (same glass system, but unspecified proportions) featured firing temperatures around 600°C or even lower. In the latter work, a piezoresistive response was actually measured, albeit with not very well defined conditions (uniaxial vertical loading with unspecified degree of lateral clamping). Nevertheless the obtained sensitivities were comparable to those obtained by us for isostatic pressure loading of standard DuPont 2041 TFRs [43], indicating promising piezoresistive properties.

An important aspect in TFRs is compatibility with appropriate terminations. As our previous work indicated some issues with Au, we analyse here the situation for both Au and Ag in detail (figure 4), on Al$_2$O$_3$ substrates and as a function of firing temperature and using the same glass: Bi12 (table 1), used both as a frit for Ag and to make the resistor (Bi12 + 11% mass RuO$_2$). The Au, on the other hand, was a standard commercial composition, ESL 8837 pre-fired at 850°C [63].

![Figure 4. Sheet resistivity at 25°C and its temperature coefficient (HTCR, 25-100°C) vs. resistor length and firing temperature (the lines are only guides to the eye).](image)
The results show that excellent compatibility is achieved with both Ag and Au. As expected, termination effects on Au are very low, while a moderate normal termination effect (negative deviation of value) is seen with Ag. This behaviour contrasts with our previous studies on the analogous lead-based low-firing systems, where "inverse" size effects tended to occur [52]. Moreover, reasonable properties are here easily achieved for firing temperatures above ca. 550°C, without the use of additives!

3. CONCLUSIONS

In this work, the chemistry and physics of standard TFRs – based on PbO-B₂O₃-SiO₂ glass with a dispersion of RuO₂/ruthenate conductive phase – were first reviewed, with an emphasis on their application to piezoresistive sensors with a metallic elastic body. It was found that glasses based on the Bi₂O₃-ZnO-B₂O₃-SiO₂ system may potentially be used in lieu of the traditional lead-bearing frits. This includes low-firing compositions, enabling deposition of lead-free TFRs on important substrates such as high-strength steel (high-performance piezoresistive sensors), glass or even aluminium alloy.

Before such novel TFRs can be applied commercially, however, many aspects still need to be examined carefully, such as CTE matching, tuning of properties (including with additives), laser trimming and general processing behaviour, and stability. Moreover, assorted materials – dielectrics, conductors and overglazes – also need to be developed.

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