Development of low-firing lead-free thick-film materials on steel alloys for piezoresistive sensor applications

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Abstract

Piezoresistive sensors based on steel and other metallic substrates provide higher strain response than on standard ceramic substrates and are more easily packaged. But exposing high-strength steels to the standard high-temperature 850°C thick-film firing cycle affects their mechanical properties. In previous studies, we have developed a range of low-firing thick-film materials based on lead borosilicate glass, which allows processing at low temperatures. However, it is desirable to develop alternatives to potentially toxic lead-based glasses that to not include alkali metals, which degrade high-temperature insulation characteristics of dielectrics. To this end, this work concerns investigations in essentially substituting lead for bismuth, and presents a series of low-melting Bi-B-Zn-Si-Al oxide glasses having good stability against devitrification. However, these glasses, when formulated as thick-film pastes using standard vehicles based on ethylcellulose binders, were found to be quite sensitive to incomplete binder burnout, with strong bubble generation within the layer. Therefore, a novel organic binder based on polypropylene carbonate, featuring clean low temperature burnout, had to be introduced. On this basis, thick-film dielectric compositions have then been developed and tested, aiming to optimise the mechanical strength and their expansion matching with the steel substrates. In the goal of a complete materials system, first tests on compatible conductors and resistors, using the same glasses, are presented as well.

Key words: thick-films, lead-free, bismuth glass, steel, sensor

Introduction

Piezoresistive sensors based on thick-film technology deposited on ceramic substrates have found success due to their low production cost. However, alumina is not optimal for piezoresistive sensing applications due to its brittleness, high elastic modulus and rather low strengh [1]. Additionally, the applications of this kind of sensors remain limited because their assembly requires elastomer seals. Stainless steels and other metals [2] potentially offer much better strength and toughness, hermetic assembly by welding and machinability [3,4].

However, the high firing temperatures associated with commercial thick-film processing (850°C) are not compatible with high-strength steel, owing to degradation of mechanical properties due to annealing or dimensional changes associated with martensitic transformation (which tend to destroy the thick-film layers). In order to avoid this problem, a solution resides in developing a thick-film system with a lower firing temperature, ideally below ca. 650°C, a temperature still compatible with good strength retention and that avoids phase transformations. In previous studies [5,6,7,8,9,10], we have developed and studied several low-firing systems based on low-melting lead borosilicate glasses, where the composition was adapted to achieve compatibility with steel substrate. Such systems need also to be thermally matched to steels, which have a range of thermal coefficients of expansion (TCE) from 11 ppm/K to 17 ppm/K, compared to standard thick-film materials, which are thermally matched to alumina (7 ppm/K).

The lead content of these materials is a problem, as lead is restricted under the European Union RoHS (Restriction of Hazardous Substances) directive [11]. Although its use in glasses for electronics applications is mentioned under the list of exemptions, this may change in the future, and further restrictions are therefore likely in the medium term.

Bismuth is a potential alternative to lead, and bismuth-based frits for thick-film conductors – albeit with a somewhat high alkali content – were already patented in 1960 [12]. Inoue [13] formulated alkali-free conductor frits implicitely, by mixing Bi_2O_3 with ZnO-B_2O_3-SiO_2 glass. The resulting "modern" Bi_2O_3-ZnO-B_2O_3-SiO_2 system, with optional MgO, BaO and Al_2O_3 additions was disclosed in several Soviet patents [14, 15, 16]. These glasses have a high Bi content, processing temperatures down to ca. 500°C, and are therefore useful as sealing glasses and frits. A limited volume of recent work specifically mentions their use or that of similar glasses in the fabrication of thick-film resistors as well [17, 18], which were found to have interesting piezoresistive properties from preliminary investigations [19].

In this work, we present the results of the development of a range of bismuth glasses and the first investigations of new low-firing lead-free thick-film system, including dielectrics, conductors and resistors. The sheet resistance (SR) and temperature coefficient (TCR) of a bismuth-glass – RuO_2 resistive composition are examined as a function of the processing conditions, the underlying dielectric, the substrate and the conductor termination.

Experimental

The following substrate materials were used: 96% pure alumina (Kyocera, Japan, A-476, TCE = 7 ppm/K) as standard thick film substrate and ferritic stainless steel 1.4016 (TCE = 11 ppm/K, comparable to the high-strength precipitation hardening martensitic stainless steels).

The thick-film materials used in this work as matrix for the dielectrics, the conductor and the resistor are based on the lead-free Bi-B-Zn-Si-Al oxide glasses.

Glass	Bi8	Bi12	Bi16	Bi9	Bi11	Bi17
Bi_2O_3 (%mol.)	45	40	50	50	45	50
B_2O_3 (%mol.)	35	35	35	30	30	25
ZnO (%mol.)	10	15	5	10	15	5
SiO_2 (%mol.)	6	6	6	6	6	6
Al_2O_3 (%mol.)	4	4	4	4	4	4
Sintering Temp. [C]	475	475	475	450	450	450

Table 1 : Bismuth glasses composition

Two dielectric types were tested: in the first one, glasses were filled with 30% mass. alumina (Alfa Aesar, aluminium oxide alpha, 99.99%, 1 μm), which is relatively inert and therefore has limited chemical reactions with the glass or piezoresistor material. However, alumina decreases the TCE of the thick-film, which could result in excessive compressive stress on steel substrates. In order to match the TCE of the thick-films to the substrate, strontium titanate ($SrTiO_3$, AlfaAesar. 99+%) was tested.

The conductor (AgBi12) is composed of Ag powder (Alfa Aesar. 99.9%, APS 0.5-1 μm) and 10% vol. Bi12 glass binder. It was fired at different temperature before (prefired) or after the resistors (postfired). A commercial gold conductor, ESL 8837, was also used to characterise the resistive composition on bare alumina.

First tests of the dielectric as a basis for the low-firing commercial 10 kΩ resistive composition ESL 3114 were unsuccessful; excessive melting and spreading of the resistor – and unusable resistance values – were observed (Figure 1). Obviously, the reaction product between both glass types gives a very low-melting mix; these materials are incompatible.

Therefore, we extended our study to resistors as well. The studied resistive composition is based on the bismuth glass Bi12 filled with 11% by mass RuO_2 powder (Aldrich. 99.9%, 40nm). The resistors were fired for 10 min at peak (45 min total cycle) at different temperatures from 500 to 625°C.

The organic vehicle is composed of 25% mass polypropylene carbonate (binder) in 75% mass. propylene carbonate (solvent).

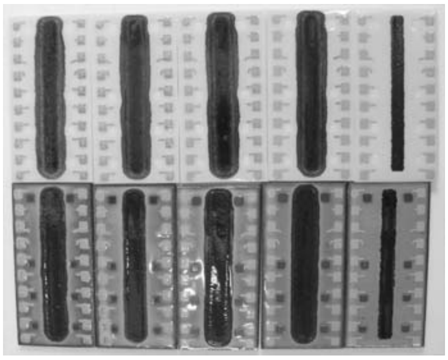

Figure 1: ESL 3114 resistors fired on bismuth dielectric alumina and steel @ 625°C

The bismuth glass – RuO_2 resistor was characterised on bare alumina (reference substrate) with three terminations schemes: a) commercial Au ESL 8837, pre-fired at 850°C; b) pre-fired AgBi12 conductor; c) post-fired AgBi12 conductor, i.e deposited onto the resistors, in light of our previous results with low-temperature lead-based glasses [8].

Following these tests, the resistor was characterised on both Al_2O_3-filled and $SrTiO_3$-filled dielectrics, deposited on alumina or stainless steel. Both (b) and (c) AgBi12 termination schemes were examined for the Al_2O_3-filled dielectrics, and only (b) was used for the $SrTiO_3$-filled ones. Samples prepared with scheme (b) were also refired at the 500°C conductor post-firing temperature used in scheme (b) for comparison of both schemes, in order for the resistor to experience the same heat treatment sequence.

Samples for electrical characterisation (sheet resistance SR and temperature coefficient of resistance TCR) were 1.5 mm wide resistors of several lengths (Figure 2), and were measured at 30°C, 65°C and 100°C.

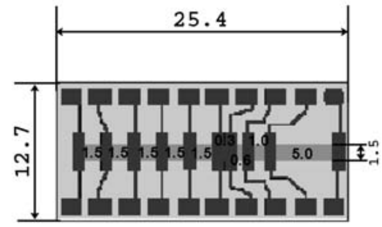

Figure 2: Layout of the test sample for measurement of electrical properties.

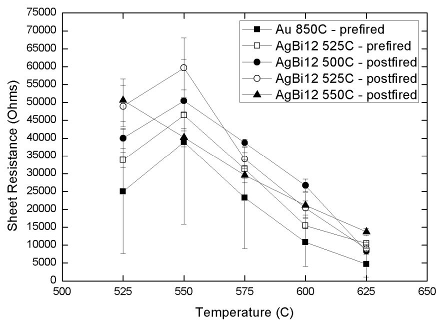

Figure 3: Sheet resistance of Bi glass – RuO_2 resistors as a function of the resistor firing temperature for different termination schemes and firing temperatures, on bare alumina.

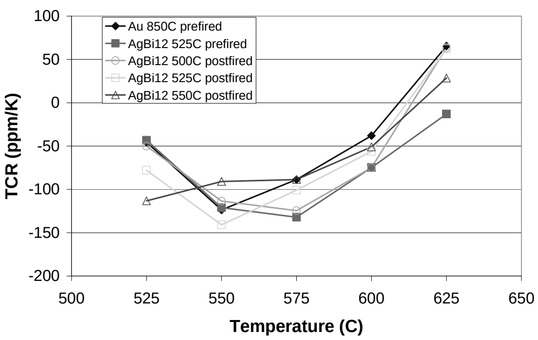

Figure 4: TCR of the resistors on bare alumina substrate.

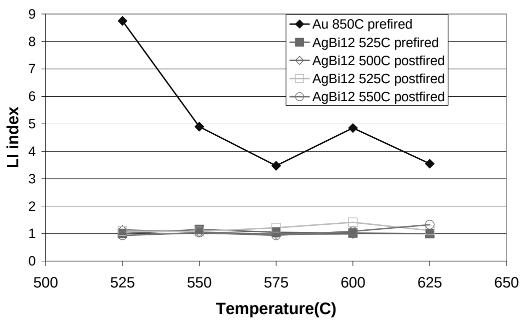

Figure 5: Length index LI the resistors on bare alumina substrate.

In order to have a quick assessment of the termination effects, we calculated a "length index" LI, defined as the ratio of the average sheet resistance of the three short resistors (0.3, 0.6 and 1.0 mm length) to the average of the 1.5 mm long ones. LI values greater than 1 imply the existence of highly resistive zones near the terminations, whereas the other case (LI < 1) corresponds to a locally decreased sheet resistance near the terminations.

Results and discussion

The results of the first characterisation of the resistor deposited directly on bare alumina substrates are depicted on Figure 3 (SR) and Figure 4 (TCR). For post-fired conductors, (scheme c), three post-firing temperature (500, 525 and 550°C) were used in order to identify the most favourable one for the next tests.

The sheet resistance is higher with the AgBi12 conductor than the gold conductor. TCR values are surprisingly moderate for a resistor series without additives, and are close to zero at firing temperatures near 600°C.

Figure 5 allows to study the terminaison effect on the resistance, and immediately show that the gold conductor is incompatible with the bismuth-glass – RuO_2 resistor, giving very strong inverse termination effects suggesting the occurrence of an insulating zone at the conductor-resistor interface. This problem is absent with pre-fired AgBi12 conductors. For post-fired AgBi12, the higher firing temperatures give an inverse termination effect, although it is totally overshadowed by the effect with Au; 500°C is therefore the preferrable post-firing temperature and was therefore used for the next tests.

The bismuth resistance was then charaterised on the both dielectric types (Al_2O_3 or $SrTiO_3$-filled bismuth glasses), themseleves deposited onto alumina or steel.

The consistence of the dielectrics was too glassy; when subsequently firing the conductors and resistors, extensive re-softening of the dielectrics occurs, leading to breakages in the conductor tracks. In an effort to alleviate this problem, conductor and resistor were fired at a temperature 25°C lower than the firing temperature of the dielectric, hence the shifted 500…600°C resistor firing temperature range (compared to 525…625°C on bare alumina). In spite of this measure, problems with the conductor tracks still occurred.

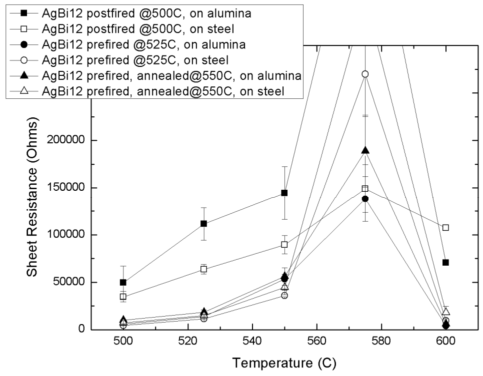

Figure 6: Sheet resistance of the resistors on dielectric filled with Al_2O_3, as a function of the resistor firing temperature, for different firing temperatures and processes of the conductor.

The Figure 6 allows to determine the firing process of the conductor. The comparison has been made on the Al_2O_3-filled dielectric based on the Bi8 bismuth glass. For the post-fired AgBi12 the sheet resistance on alumina subtrate is unreliable: the resistors are apparently cracked (most likely due to cracking in the dielectric), and no meaningful measurements are possible. On the contrary, on the steel substrate, the results are very reproducible, but markedly different from those observed on bare alumina (Figure 3). While some evidence of a peak of SR for firing temperatures around 550°C is seen on bare alumina, a much stronger peak, rather centred at 575°C, is seen on dielectric. The peak of resistor value vs. firing temperature have been observed previously by Kubový et al. [20]; they attributed it to the transition between a wetting phase of the conducting powder by the glass (which moves the particles apart and therefore increase SR) and a phase where diffusion from the conductive particles into the glass progressively decreases SR. Similar effects were also observed by us in our previous studies of low-firing lead-based glass – RuO_2 resistors [21,22]. In our case, the shift to higher temperatures and increase of magnitude of the peak could be due to excess glass moving out of the dielectric into the resistor, a hypothesis that must still be considered as speculative, although the dielectrics do look more glassy at high firing temperatures. On the other hand, this peak is definitely not due to the substrate, as it is observed on both alumina and steel.

Annealing the films at 550°C results in a moderate and reproducible increase of SR for all firing temperatures.

Figure 7 depicts the sheet resistance of the resistor on the Al_2O_3-filled dielectrics based on the 6 bismuth glasses deposited on steel substrate. The conductor AgBi12 is prefired on these samples. A more glassy appearance is visible starting at ca. 550°C firing temperature for all dielectrics, and all curves exhibit a peak of SR for a firing temperature of 575°C.

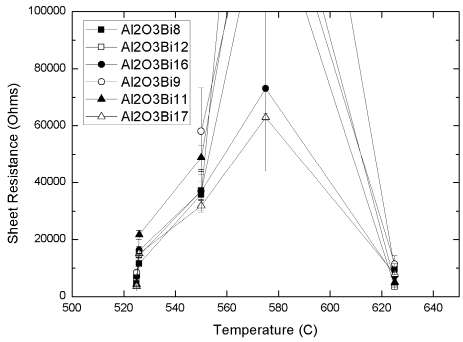

Figure 7: Sheet resistance of bismuth resistance in function of the firing temperature of the resistance on dielectric filled with Al_2O_3 based on different bismuth glasses.

The $SrTiO_3$-filled dielectrics, which should have better TCE matching with the steel substrate, gave results different from the Al_2O_3-filled ones. First, only 3 bismuth glasses suited were compatible with $SrTiO_3$: Bi8, 12 and 16. The three other react with this filler (Figure 8) or crystallise in contact with it. It is interesting to note that there is a good correlation between glass stability and compatibility with $SrTiO_3$; the three compatible glass lie comfortably inside the stability zone of glass formation, while the three incompatible ones lie at the composition boundary with glasses that crystallise too rapidly to be useful as frits

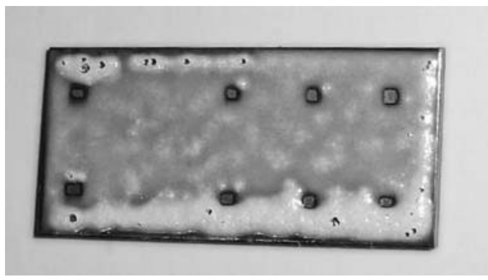

Figure 8: Stability problem with $SrTiO_3$-filled Bi9 dielectric

Figure 9 depicts the sheet resistance of resistors on steel substrates with AgBi12 prefired conductor. As expected from the high TCE imparted by $SrTiO_3$, the dielectrics cracked on alumina, and no meaningful measurements could be made on this substrate in the case of $SrTiO_3$-filled dielectrics.

With the compatible glasses, we obtain values similar to that on alumina-filled dielectrics for low firing temperatures (≤550°C), but the peak of SR at 575°C and subsequent drop at 600°C are much less pronounced on the $SrTiO_3$-filled dielectrics. The TCR (Figure 10) values are not too different from those observed on bare alumina substrates – they are also quite close to zero, given the fact that no TCR-driving additives were used.

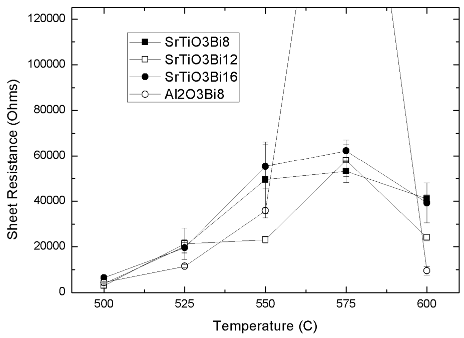

Figure 9: Sheet resistance of bismuth resistance in function of the firing temperature of the resistance on dielectric filled with $SrTiO_3$ on steel substrate.

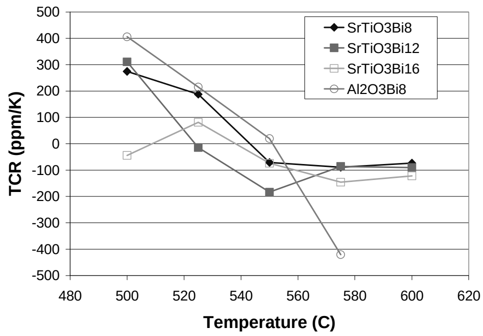

Figure 10: TCR of bismuth resistance in function of the firing temperature of the resistance on dielectric filled with $SrTiO_3$ on steel substrate.

Conclusion

In this first study of thick-film materials based on low-firing glasses with bismuth as a replacement for lead, functional dielectric, conductor and resistor compositions could be formulated, and the resulting resistor properties were very promising, with SR in the 10…100 kΩ range and low TCR values even without using TCR drivers. Both Al_2O_3-filled dielectrics (better chemical compatibility) and $SrTiO_3$-filled ones (better TCE matching to steel) were successfully used.

These results were achieved at firing temperatures below 650°C, and thus we can safely assert that a low-firing thick-film system compatible with high-strength steel for piezoresistive force and pressure sensing is possible (the existence of appreciable piezoresistivity was confirmed by manually bending the resistive test patterns, but no quantitative measurements were made).

The main current issue is the stabilisation of the dielectrics, in order to avoid softening upon re-firing. This may be carried out by controlled reaction and / or cristallisation of the glass in contact with the filler. More extensive studies will of course also be carried out on the resistor materials in the future, including characterisation of their piezoresistive properties.

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