The 4th KIMM-EPFL-IIS Joint Workshop on Micro/Nano Mechatronics and Production Technologies, October 11-12 2004.

Low-Temperature Thick-Film Systems for Electronic and Sensor Applications

Thomas Maeder, Claudio Grimaldi, Sonia Vionnet, Caroline Jacq, Hansu Birol,
Sigi Strässler and Peter Ryser

Institut de Production et Robotique, Laboratoire de Production Microtechnique (IPR – LPM)
Ecole Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland

ABSTRACT

This paper presents recent work on complete thick-film systems, including dielectrics, conductors and resistors, with a lowered firing temperature range of 450…750°C. These materials allow the extension of proven, reliable and inexpensive thick-film technology to novel applications in electronics and sensors.

Key Words : thick-film systems, low-temperature processing, electronics, sensors.

Nomenclature

TCR = temperature coefficient of resistance (in general)
HTCR = TCR, measured between 25°C and 100°C
CTE = coefficient of thermal expansion

1. Introduction

Thick-film electronics have been applied since a long time [1] for applications requiring high stability and reliability. More recently, thick films have been applied in sensorics, especially for piezoresistive and chemical (mainly gas) sensors. Chemical sensors normally use special, porous compositions as the active material, whereas piezoresistive ones typically use commercial thick-film resistors [2].

Thick-film resistor compositions consist of a dispersion of conductive nanoparticles, usually RuO_2, $Pb_2Ru_2O_6$ or $Bi_2Ru_2O_7$, in an insulating lead borosilicate glass matrix. Their resistive and piezoresistive properties are governed by a percolation mechanism where conduction between adjacent particles occurs by tunnelling [3,4].

Standard thick-film processing involves three phases: 1) deposition by screen-printing, 2) drying at ca. 150°C, and 3) firing. Over time, a "standard" firing profile with a 850°C peak temperature has emerged for conductors, dielectrics and resistors, which essentially restricts thick films to high-temperature substrates such as alumina. While some specialised pastes exist which can be fired at lower temperatures, no complete thick-film system, including compatible conductors, dielectrics and a resistive series, is available. Such a system would open up several new applications for thick-film technology.

- Force & pressure sensing on steel, Ti or Al alloys, which have vastly superior elastic properties to alumina.
- Electronics on glass for displays and optical devices (Fig. 1).
- High power electronics or heaters on Al.

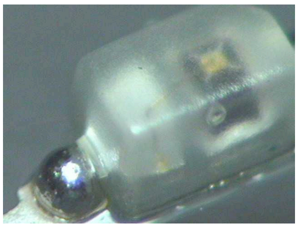

Fig. 1 Diode soldered on glass substrate, using commercial low-temperature Ag conductor.

The development of a complete thick-film system with a low firing temperature entails several issues, one of the most troublesome being achieving a good burnout of the organics before sintering of the layers.

- **Conductor**. This is the easiest requirement to fulfill, e.g. by using silver with a low-temperature glass frit (available commercially).
- **Dielectric**. Low-temperature glasses cannot act as dielectrics, as they re-melt upon firing of the subsequent layers, interdiffusing excessively with them. Therefore, they must be stabilised by crystallisation or by using an appropriate filler.
- **Resistors**. Developing low-temperature resistors involves using a glass with a low softening temperature, which entails several potential issues such as increased CTE and lowered chemical reactivity / different phase equilibria.

This paper presents recent work at our laboratory towards achieving such a low-temperature thick-film system, and a few applications thereof.

2. Low-temperature thick-film system

2.1 Glasses for dielectrics & resistors

Glasses were made within the lead-rich portion of the $PbO \cdot B_2O_3 \cdot SiO_2$ (lead borosilicate) glass system (Fig. 2), which is the usual matrix for thick-film resistors [1]. We have examined the compositions labelled 1, 3 and 5. The compositions are given in Table 1. 2% mass Al_2O_3 was added to inhibit crystallisation [5].

We chose to use the same parent glasses for dielectrics and resistors in order to improve chemical compatibility.

No	PbO % mass	B_2O_3 % mass	SiO_2 % mass	Firing range °C
3	63	25	12	650-750
1	75	10	15	525-600
5	85	10	5	450-550

Table 1 The selected glass compositions (2% Al_2O_3 added to inhibit crystallisation).

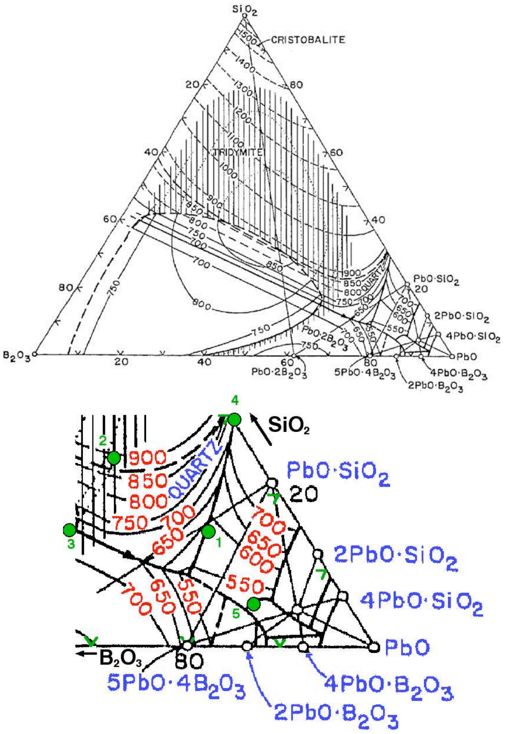

Fig. 2 Melting points in the lead borosilicate glass system [6] (compositions in % mass; white SiO_2-poor zone = decomposition into two phases). The studied glass compositions (green numbered dots) within the lead-rich portion of the diagram are shown in the lower figure.

2.2 Resistors

Resistor pastes were prepared using a three-roll mill, by mixing the glass and RuO_2 powder in various proportions, together with an organic vehicle. Resistors were then screen printed on substrates & gold terminations and fired in air at different peak temperatures. Data are presented here in Fig. 3 for resistors based on glass no 1 loaded with 40 nm RuO_2 powder, and fired at 525…675°C.

Resistance of the glass without RuO_2 is extremely high. Adding increasing RuO_2 contents doesn't reduce it significantly until a percolation threshold, which is located around 5 volume% and depends on several parameters such as particle sizes, glass composition and firing temperature. Above this threshold, resistance decreases, TCR increases and the gauge factor decreases.

The very large TCR range of these model compositions indicate that TCR modifiers must be used to achieve practical resistors with a TCR around 0.

The gauge factor of a typical 10 kOhm composition (8% RuO_2) is around 15, which is very satisfactory. Therefore, these low-temperature resistors have the potential to be applied in force and pressure sensors.

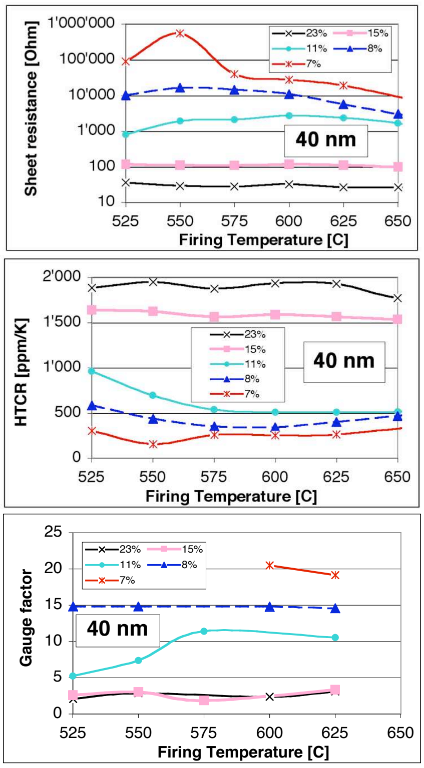

Fig.3 Sheet resistance, HTCR and longitudinal piezoresistive gauge factor of no 1 glass loaded with various volume% of 40 nm RuO_2 powder, data from [7].

2.3 Dielectrics

Three fillers were used to stabilise the glasses: Al_2O_3, SiO_2 and TiO_2. In our firing range, Al_2O_3 is essentially unreactive, e.g. no significant dissolution into the glass is expected. This is not the case for SiO_2 or TiO_2, which both may react with the glass in the following way.

SiO_2 + glass → SiO_2-rich glass
TiO_2 + glass → PbO-poor glass + $PbTiO_3$

Fig. 4 shows the conversion rate of the reaction of glass no 1 with TiO_2. Using nanosized powders, stabilisation can be successfully achieved around 600°C, allowing application onto glass, Ti and Al alloys.

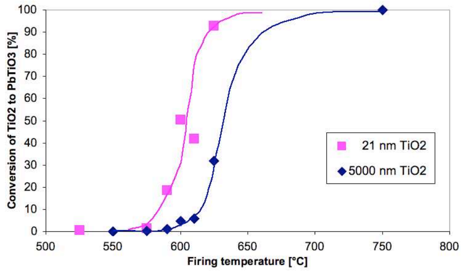

Fig. 4 Conversion of TiO_2 to $PbTiO_3$ in glass no 1, measured by X-ray diffraction.

These additions yield dielectrics with improved stability compared to passive fillers such as Al_2O_3. However, this is gained through a change in the glass composition, which now can react with resistors and alter their properties. This is shown in Fig. 5 below for a typical resistor on two dielectrics stabilised with TiO_2, where a strong alteration of the resistor's TCR occurs although the resistor and the dielectric share the same parent glass.

Besides dimensional stability and chemical compatibility, dielectrics must fulfil additional requirements such as CTE matching and adhesion to the substrate. This is a challenging task given the very wide CTE range of potential substrates (pyrex: 3.3; alumina: 7, float glass & Ti: 8; ferritic steel: 11, austenitic steel: 17, Al: 23 ppm/K) and their widely differing chemistry.

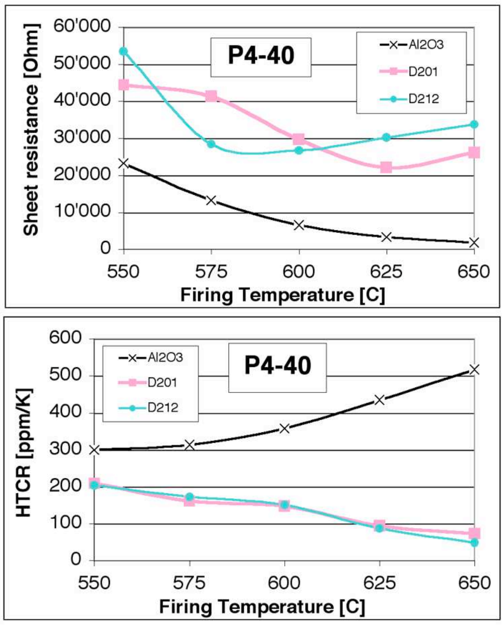

Fig.5 Sheet resistance and HTCR vs. firing temperature of thick-film resistor (glass no 1 + RuO_2), directly on Al_2O_3 substrate and on two dielectrics (D201 & D212, glass no 1 + TiO_2).

3. First applications

3.1 Knee force sensor – upper layers

This device (Fig. 6) allows measurement of ligament force and torque balance in total knee arthroplasty operations [8]. It was fabricated using standard thick-film technology on a biocompatible austenitic steel. However, excessive thermal mismatch stress build-up due to the very high CTE of this steel (17 ppm/K) and to the large number of required layers led to occasional mechanical failure of the thick-film structure and hence to poor reliability. The upper layers of the device (crossover dielectric, top conductor and overglaze) were therefore successfully replaced by the new low-temperature pastes, which allow a much lower stress. The ultimate goal is to obtain a fully low-temperature thick-film structure, in order to avoid softening the steel by excessive heating.

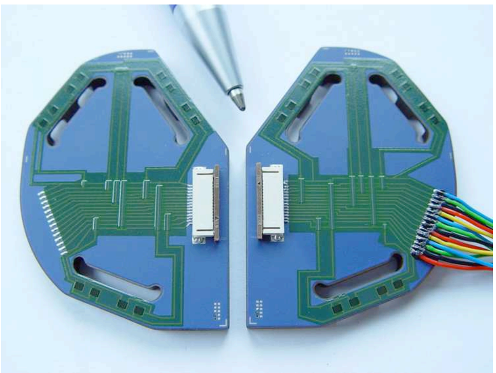

Fig. 6 Ligament balancing knee force sensor for total knee arthroplasty.

3.2 Hot plate on Al

This hot plate (Fig. 7), with temperature stability > 300°C, demonstrates the potential of the new low-temperature dielectrics, applied here with a commercial fritted Ag conductor as a heating track. The currently used glass + TiO_2 dielectric exhibits outstanding stability, but too high stress on Al alloys due to a low CTE (ca. 6 vs. 23 ppm/K). Work is underway to alter its composition by suitable fillers, or to use Al–Si composite substrates, which have much lower CTE values.

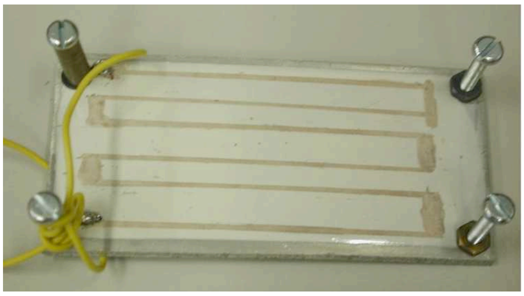

Fig. 7 Bottom side of prototype thick-film hot plate.

3.3 Prototype force sensor on Al

This prototype demonstrates a complete thick-film piezoresistive force sensor on a 6082 Al alloy substrate. The prototype, its piezoresistive response and drift are shown in Fig. 8.

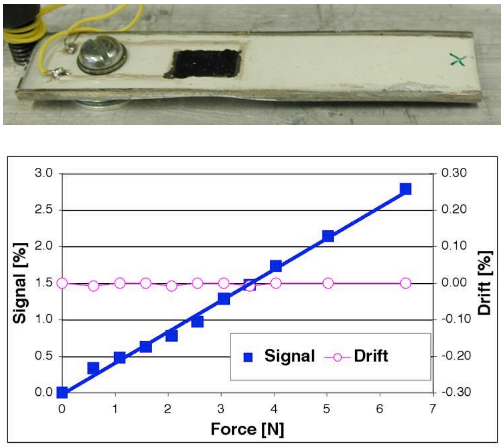

Fig. 8 Experimental thick-film force-sensing beam on 6082 Al alloy & piezoresistive response, from [9]

4. Conclusions

Considerable progress has been made towards achieving thick-film materials systems with lowered processing temperatures (450…750°C vs. 850°C). This opens up a wide range of applications for thick-film technology in electronics and sensors.

Now that the potential of these new materials has been demonstrated, future work will concentrate on studying and improving the properties of the resistors (temperature dependance, stability, trim behaviour) and dielectrics (stabilisation, adhesion on and TCE compatibility with substrates) while maintaining good chemical resistor – dielectric compatibility,

Acknowledgments

The authors gratefully acknowledge the support of the Swiss Government through its CTI and TOP Nano 21 programmes.

References

1. Coleman-M, "Thick-film materials for hybrids", The Radio and Electronic Engineer 52 (5), 227-234, 1982.
2. Prudenziati-M Morten-B, "The state of the art in thick-film sensors", Microelectronics Journal 23, 133-141, 1992.
3. Carcia-PF Ferretti-A Suna-A, "Particle size effects in thick film resistors", Journal of Applied Physics 53 (7), 5282-5288, 1982.
4. Grimaldi-C Maeder-T Ryser-P Stässler-S, "Segregated tunneling-percolation model for transport nonuniversality", Physical Review B 68, 024207, 2003.
5. Prudenziati-M Morten-B Forti-B Gualtieri-AF Dilliway-GM, "Devitrification kinetics of high lead glass for hybrid microelectronics", International Journal of Inorganic Materials 3, 667-674, 2001.
6. Johnson-DW Hummel-FA, "Phase equilibria and liquid immiscibility in the system PbO-B_2O_3-SiO_2", Journal of the American Ceramic Society 51 (4), 196-201, 1968.
7. Vionnet-S Grimaldi-C Maeder-T Ryser-P Stässler-S, "Study of electrical properties of piezoresistive pastes and determination of the electrical transport ", Journal of the European Ceramic Society in press, 2005.
8. Crottet-D Maeder-T Fritschy-D Bleuler-H Nolte-LP Pappas-IP, "Validation of a force- and location-sensing device designed to improve the ligament balancing procedure in total knee arthroplasty ", IEEE Transactions on Biomedical Engineering in press, 2004.
9. Vionnet-S Grimaldi-C Strässler-S Maeder-T Ryser-P Hofmann-H, "Nano grain thick-film pastes for mechanical sensor applications", Poster Session, Nanofair, International Fair and Conference, St-Gall, Switzerland, 2003.