Microfluidic Sensors using LTCC Technology for Environmental Monitoring Applications

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Abstract The lab-on-chip testing units are booming nowadays, due to robustness, simplicity of use and reliability. Multilayer nano-ceramic technology, functionalized with sensing materials at nano-scale, and further developed towards obtaining microfluidic test elements for environmental applications, represents the purpose of the paper.

Keywords: LTCC; multilayer nano-ceramic; microfluidic test elements; environmental applications

1. Introduction

Microscale sensors have been widely developed by microfabrication and integrated into microfluidic devices, due to their demand for rapid chemical analyses in miniature formats at point-of-need, offering advantages as: quick analysis, low usage of reagents and low level of hazard. Development of microfluidic devices has often used techniques based on silicon lithography from the semi-conductor industry, but these are expensive and not always readily available, or by polymer multi-layer technology, by placing sheets of monomers in a small mold on a microscope slide and polymerizing them by exposure to UV light, the letter ones being complicated as procedure and unreliable. The sensors market and industry have grown constantly over the past years, putting pressure on the development of new concepts and technologies. Low Temperature Co-fired Ceramics (LTCC) have become an attractive technology for electronic components and substrates that are compact, light, and offer high-speed and functionality. Multilayer ceramics can be functionalized with nano-scaled sensing materials and further integrated within microfluidic test elements, but the technology and materials for such applications are in the early development phase. On the other hand, LTCC technology represents a low cost, high performance solution for the ceramic applications, which can provide a promising impact upon the bio-chemical and medical devices technology. The result will be one system to provide all of the possible required analyses for a given type problem, with all processing steps performed on the same chip, with no user interaction required except for initialization, in terms of portable bedside systems. Lab-on-chip testing units based on microfluidic features and integrating sensors in LTCC-technology may represent a sustainable response for chemical analyses in environmental applications.

2. LTCC Technology

Low-Temperature Co-fired Ceramic (LTCC) has been used for many years for highly reliable interconnections technology in the electronics industry and it is still considered as one of the more suitable technologies for the fabrication of 3D ceramic microsystems. The thick-film technology is used for the lateral and vertical electrical interconnections, and for generating embedded and surface electronic components, such as resistors, thermistors, heaters, inductors, capacitors, piezoelectric devices etc.

The technology presumes: laser-mechanically shaping of 'green' (un-sintered) ceramic foils; punching/cutting of circuit lines as very small holes and filling them with conductive paste afterwards; screen-printing of lateral conductive patterns in thick-film technology; stacking and laminating together all individual layers by hot pressing, according to a predefined 3D architecture; sintering the obtained laminate in a singular process (co-firing) at lower temperatures (up to 900°C) to form a rigid monolithic ceramic multilayer circuit (module), Figure 1. The firing process involves: a firing phase (at 200÷400°C), when the organic binders and solvents burn out; a main co-firing phase (at 700÷900°C), when the metal particles are sintered and the glass particles are melted; a controlled cooling phase in a pre-defined environment and duration, an example being presented in Figure 2, [1, 2]. Material selection is a crucial part of microfluidic system development because it impacts the processing, functionality, application and disposability of the sensor designations.

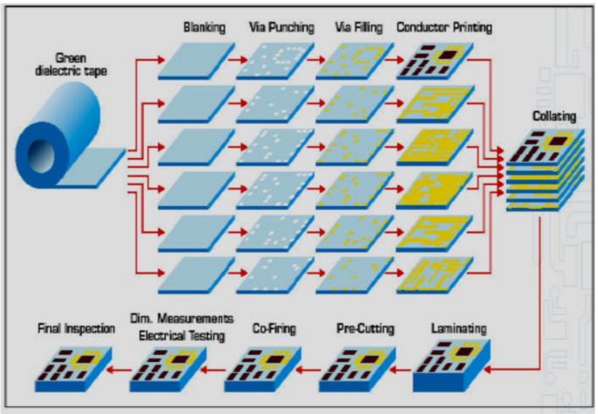

Figure 1. Example of LTCC technological line

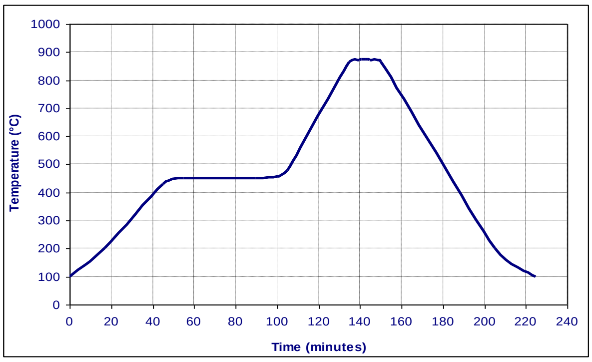

Figure 2. Example of LTCC firing process

The functional aspects such as capillary forces in micro-channels, hydrophobicity and nonspecific adsorption of the sample analyte are achieved by an optimal balance between the materials and processing conditions. Other technical concerns are related to corrosiveness, temperature isolation and interaction with chemical environment. The ceramic support is usually an alumina/silicate mixture with a glass frit and an organic binder. The layer to be printed on ceramic support is obtained as a functional ink, based on metallic or ceramic nano-powders with plasticizers, in organic solvents. Studies upon the compatibility of nano-materials within inks for screen-printing and LTCC support were also performed.

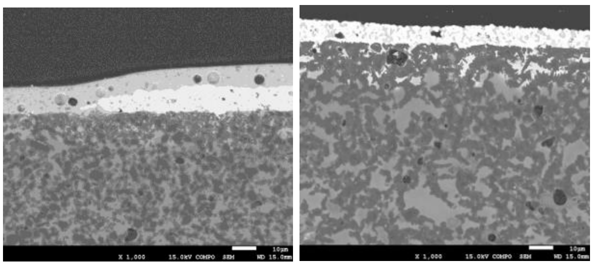

Figure 3.LTCC layer (cross-section) with resistive/conductive part above

3. Nano-ceramic sensor design

The sensor with different geometrical configurations is designed by use of COMSOL Multiphysics software, [3]. The most sensitive configuration of sensing area is generated as integrated interdigit capacitance, and the simulation is needed to determine a formula for calculating the capacitance of the sensors with different number of fingers, different lengths, widths and spaces between fingers, in relation with the thickness and permittivity of the layers. Details about the concept design, algorithms and results are presented in [4], and in Figure 4.

According to the simulation results vs. technological limits of fingers dimensions, the imposed fingers widths and respectively space between fingers was between 0.2 ÷ 0.6 mm. It was generally noticed that higher capacitance values are obtained at lower space between fingers and larger widths, respectively at lower space between fingers and greater lengths. The highest capacitance value was achieved at a minimum 6 mm finger length, a minimally technologically feasible value of 0.2 mm for the space between fingers, and respectively at the maximum width of 0.5 mm. Under the circumstances, larger capacitance values can be obtained only by increasing the finger length up to the technological limit of 12.5 mm. Separate studies were allocated to the behavior of interdigit structure in the presence of different liquid types, for pre-determining the micro-fluidic features, in terms of wettability, surface tension, dispersability etc.

Other specific tests concerned analysis of the variation of capacitance versus frequency for the dry sensor and the wetted one, for different amounts of various liquid types (in principal distilled water, isopropanol and acetone - with relative dielectric permittivity values of 77.0, 20.7 and 18.3 respectively). A cvasi-linear dependence of capacitance with liquid dielectric permittivity was found, in accordance with the simulations for a planar capacitor formula and homologue results presented in [5], but unexpectedly the capacitance seemed to increase cvasi-linear also with the liquid amount till 25μl, due to microfluidic features of planar structure, and fluid behavior at intedigit sensor surface, a result of extremely importance for microfluidic measurements.

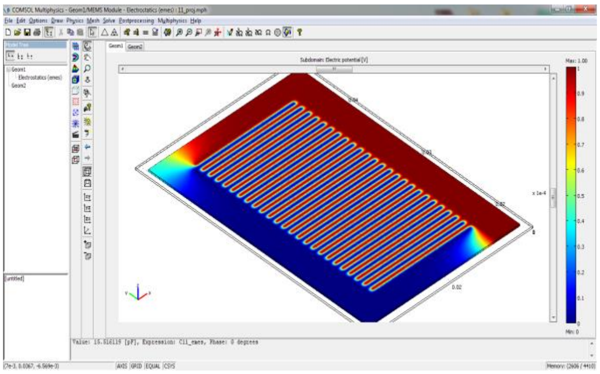

Figure 4. Simulation of interdigit sensor and capacitance response

4. Generation of LTCC microfluidic elements

The concept for embedding microfluidic features of nano-ceramic sensors is in line with homologue research as described in [6, 7], Figure 5.

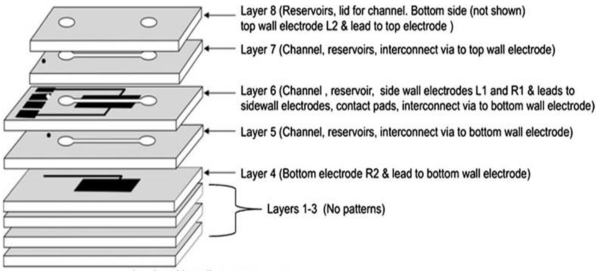

Figure 5. Embedding microfluidic features as tailored LTCC layers

Different architectural configurations were tested, as the micro-channels or valves manufacture in LTCC technology is simple, by shaping the respective layers (before the lamination). The typical cross-section of channels is rectangular, and the maximum height is determined by the thickness of the layer. Some samples of experimental microfluidic elements are presented in Figure 6.

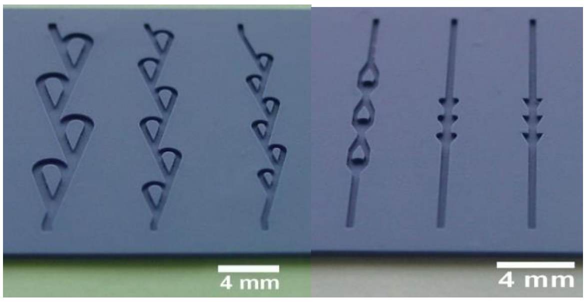

Figure 6. Microfluidic elements within LTCC layers

Finally, microfluidic simulations were performed, to emphasize the liquid flow phenomena through the channels, at different rates and viscosities, as presented in Figure 7.

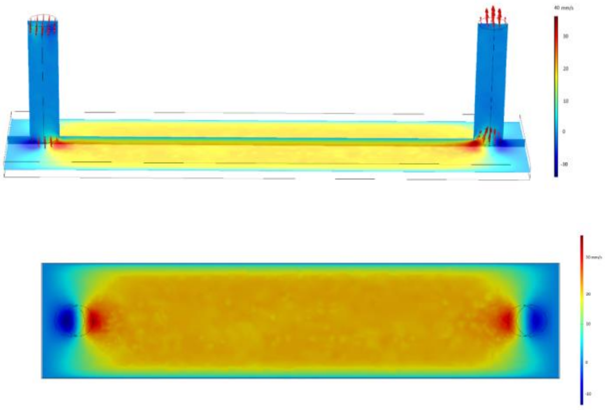

Figure 7. Microfluidic elements simulation

5. Electrochemical tests of sensors in a 'flow injection analysis' system

The prototypes of sensors with different configurations and sensing materials were tested by use of electrochemical equipment, i.e. a potentiostate.

A particular configuration of sensors output electrodes was designed, to permit a direct connection to the plug-and play connecters, as presented in Figure 8.

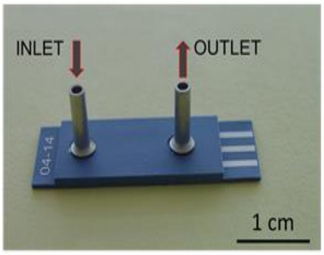

Figure 8. Microfluidic sensor and connecting system

The sensors were attached to a specialized flow injection system with peristaltic pump, reservoirs, and injection valves, as shown in Figure 9.

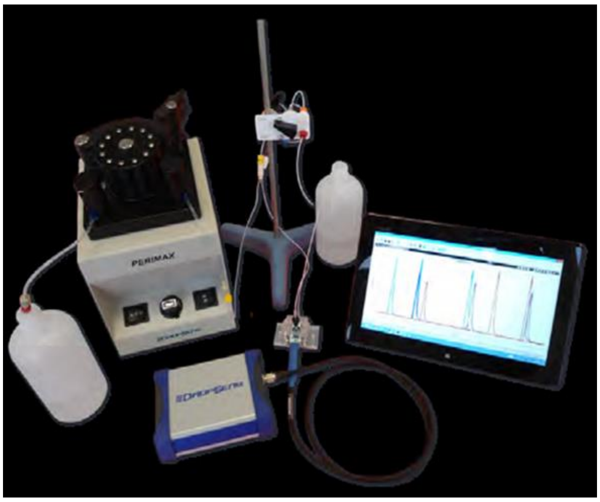

Figure 9. Electrochemical test system

The study was oriented towards proving the selectivity, sensitivity and reproducibility of sensors in different redox media. The results were very promising, both under the continuous flow of diluted analyte, or by periodically injecting of analyte of different concentrations in the support fluid, passing through the pump.

Finally, a specific test in environmental conditions was performed, for the detection of certain aromatic pollutants in water, via their reaction withFerricyanide oxidant systems. The detection limit of sensors was successfully demonstrated for concentrations less than 10^{-5}M, with high selectivity and sensitivity. The sensors design allowed not only the self-cleanable effect, but the experiments have also shown no saturation effect, or errors of measurements at different sequences, when changing randomly the analyte concentration, if min. 10 sec. between measurements are allowed, see Figure 10.

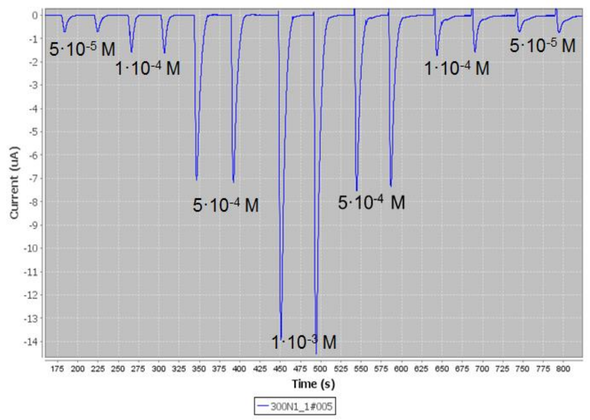

Figure 10. Electrochemicaltest results under different concentrations

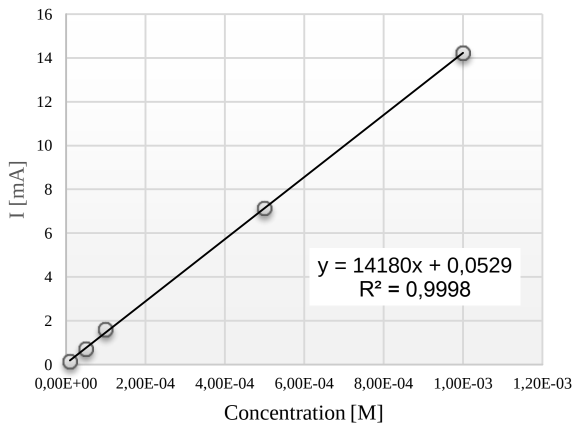

Figure 11. Electrochemical test results / calibration curve for Ferricyanide detection

The results for pollutants detection (in H_2SO_4, 0.1 M concentration; 1ml/min. flow; E_{det} = -0.20 V; interdigit sensor with Au electrodes) and the obtained calibration curve are presented in Figures10 and 11. The measurements demonstrated a high accuracy of detection of very low concentrations of liquid, with a linear calibration curve of measurements between e.g. 10^{-5}M and 10^{-3}M concentrations values. The measurements proved to be very selective in relation with aromatic pollutants, even at very low quantities of liquid (amounts from 5µl to 30µl) and/or under the presence of different interfering oxidative substances, the calibration curve presented in Figure 11 maintaining its viability in the confidence limit of 95%, if the experimental conditions are kept, i.e. if using the same support fluid.

Conclusions

The lab-on-chip testing units are booming nowadays, due to robustness, simplicity of use and reliability. Multilayer nano-ceramic technology, functionalized with sensing materials at nano-scale, and further developed towards obtaining microfluidic test elements for bio/environmental applications, represents the purpose of the paper. The concept, simulation procedure, design process and an experimental model of integrated interdigital capacitive sensors with embedded microfluidic features realized via LTCC technology are briefly presented, with very promising results. The prototypes of sensors with different configurations and sensing materials were tested by use of a potentiostate, the microfluidic sensors being attached to a specialized flow injection system with peristaltic pump, reservoirs, and injection valves. The measurements demonstrated a high accuracy of organic pollutants detection of very low concentrations, with a linear calibration curve of measurements between 10^{-5}M and 10^{-3}M concentrations values. The measurements proved to be very selective in relation with some pollutants, at very low quantities of liquid and/or under the presence of different interfering oxidative substances. The research will continue in the direction of realizing microfluidic multi-platforms for simultaneous detection of more analytes, and by providing the sensor with an embedded piezoelectric system to allow the direct admission of lower quantities of liquid without using the flow injection system, i.e. assuring the measurements portability.

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