Ink-jet printing for ceramic functional coating

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Abstract

The interest of functional ceramics coatings based on low cost and flexible manufacturing has been pushed up by the effectiveness shown by the Chemical Solution Deposition (MOD-CSD) of metal-organic salts route, based habitually on the use of spin coating, deep coating or slot die techniques previous to the thermal treatment to achieve the decomposition of the starting salts. The possibility to implement effective Drop on Demand (DoD) systems in the manufacturing process allows a more efficient way to homogeneously extend the precursor solution over the substrate, being so able to control the thickness of the ceramic coating among other manufacturing advantages as control of solvent evaporation. In this work we report on our experiments concerning ink jet coating of functional complex ceramics as LSMO over single crystalline substrates by using a single nozzle piezolectric dispenser. Characterization of both, the rheological properties of the developed ink, and the resulting coating by XR diffraction, SEM, and magnetic behavior are reported.

Introduction

Functional electroceramics coatings are in the industrial scope for obtaining operative devices with specific performances based on their singular properties. Conductive, semiconductive, piezoelectric, ferroelectric, pyrolectric, PTC, magnetoresistive, among a large etcetera of functionalities of metallic oxides have open the scope for manufacturing of devices that can be integrated with the standard electronics producing cheaper and effective devices exploiting the electrical functionalities that the world of ceramics can offer, from energy harvesting to supermarket ticketing, from sound transducers to capacitors or actuators.

Fabrication of controlled layers of functional ceramics is in the basis of the realization, at industrial scale, of devices that get profit of their singular properties giving an opportunity to develop specific manufacturing techniques which can achieve quality , flexibility and low cost. Functional ceramic coating is being produced by CVD, Sputtering, PLD and several other techniques which require high vacuum and extremely pure environment. From these expensive coats, a device can be built by using photographic techniques capable to produce the functional pattern adequate to be integrated in the full device which can be built over the same substrate. Chemical Solution Deposition has been demonstrated as an efficient way for obtaining good ceramic coats. Solutions of organic salts of the metals, corresponding to the selected ceramic, are commonly used for painting the surface of the substrate, and after pyrolyzation and growing processes, producing the coating that can be epitaxial or polycrystalline according to the properties of both, the substrate and the coating ceramic.

The way to coat the substrate with the precursor solution should achieve uniformly covering of the surface and support the the stress during thermal treatment without cracking, buckling or any alteration of the thickness of the layer being so extremely worth to control the surface properties and fluid dynamics of the precursor solution.

In the framework of the EFECTS EU collaborative project we are investigating the possibility to perform layers of $La_{0.7}Sr_{0.3}MnO_3$. This ferromagnetic complex ceramic allows achieve magnetoresistive effect and could be considered for sensing magnetic field and could be on the basis of transducers manufacturing.

Experimental

Two precursor systems have been considered. A first system based on propionates of Lanthanum, Strontium and Manganese, [1] and a second system based on acetates of the same metals [2, 3].

Deposition has been performed on, square shaped, single crystal LAO substrates of 5x5 mm^2 and 10x10mm^2 and thermal treatment was performed in a tubular oven up to 900ºC in air. From 100ºC temperature increased up to 400ºCwith a heating rate of 0.5 ºC/min, being increased to 1ºC in the following ramp up to 900ºC. The samples were maintained at his temperature during 5 h and then freely cooled down to room temperature.

Deposition was performed in a proprietary mechanical system , with controlled atmosphere, and using two kinds of single nozzle jetting devices. A first one based on electromagnetic valve with a nozzle of 100 µm in diameter, and a second one based on a glass pipette piezo electrically activated.

Propionates

Propionates of La, Mn, and Sr, have been obtained and dried in vacuum for 12 hours at 90ºC. Adequate amounts to obtain the metal stoichiometry, Mn 1, La 0.7, Sr 0.3, have been weighted in order to obtain samples of 10mL and a concentration of 0.03M in Mn, using propionic acid as solvent.

The solution presents the rheological properties summarised in table I.

Table I Properties of propionates based inks

Viscosity (mPa/s)	1.020
Surface Tension (mPa/m)	22.01
Contact angle over LAO (º)	7.60
Density (g/mL)	0.99

Due to the low viscosity of the solution, addition of ethyleneglycol has been realized in a 30% (w/w) thus increasing the viscosity up to 5.2 mPa s. To correct the increasing of wetting angle produced by the higher surface tension of the solution, 0.06% (w/w) ofTriton 114 was added (w/w) keeping so the wettability of the solution.

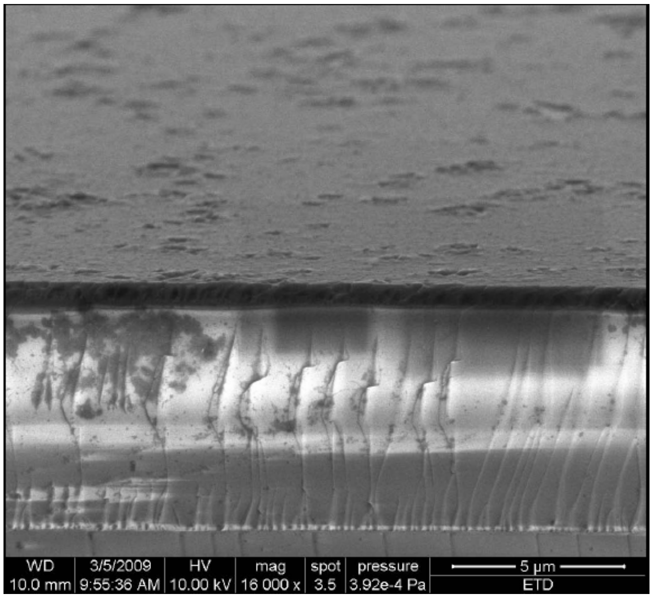

Figure1 LSMO coated LAO substrate by propionic ink

Solutions were stable for more than one month. Larger times have not been tested.

Acetates

Acetates based system was prepared by disolution acetate salts of Sr and La in water and Glycine, and Mn in water and EDTA. A solution of Ethanol and water (10-90%) and polyethyleneglycol (PEG MW 20000) was added to obtain the desired concentration. For concentration 0.038 M in Mn, the rheological properties are summarised in table II.

Table II. Properties of acetates based 0.038M ink

Viscosity (mPa/s)	3.147
Surface Tension (mPa/m)	25.3
Contact angle over LAO (º)	<7
Density (g/mL)	0.917

Solutions tend to oxidize if are in contact with air. Hermetically covered have been tested for a month.

Printing

Two kinds of printing systems have been used to test the inks. The first is an electromagnetic valve which can be open during a time in the range of 500-1000 µs, delivering so a part of the fluid pressurized in a chamber. The system allows to deliver drops of a volume in the range of tens of nanoliters according to the pressure in the chamber and the time and amplitude of the valve opening.

The second system is mounted in the same mechanics and consist of a commercial pipette with piezoelectric excitation configuring so a piezo-dispenser. The dispenser we used has a nozzle of 60µm in diameter and can deliver drops with a volume in the range of 40 pl. The volume can be tuned by controlling the amplitude and the time of the electric pulse which triggers the drop.

Electromagnetic valve

Full layer and patterned coatings have been performed showing all of them electrical conductivity with resistances in the range of 10-100kΩ as expected for LSMO. According to the drop pitch it is possible to obtain continous layers with a thickness which depends on the substrate, the concentration of the solution, and the density of the drop firing, the number of drops per surface unit. The adequate overlapping of drops should be adjusted in agreement with the drop volume and the solution used. In our case, the diameter of the drops is nearly 300 µm and good covering can be achieved with a drop pitch of 100-150 µm . In Figure 1 it is shown the LSMO continuous coating of a single crystal LAO substrate obtained by jetting propionates based solution. The thickness is in the range of 500nm and shows a good compacity.

As can be seen in figure 2, the XRD pattern show that the LSMO layer has grown epitaxially as expected from the low mismatch between the LAO and LAMO cell parameters. In the figure, it is shown the pattern for a single layer coating and a double coating obtained by an initial jetting of solution, firing, a second jetting process and a second firing, the increasing in the amplitude of the LSMO peaks is in correspondence with the increassing of thickness .

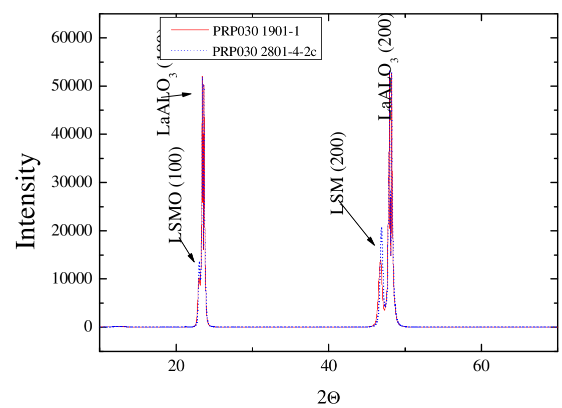

Figure 2 XRD diffraction patterns corresponding to a single and a double coating with propionates based LSMO ink.

Magnetic behaviour is also tested. Their magnetic moment has been measured at both temperatures, 300K and 10K showing the expected behaviour for this ceramic as referred in figure 3.

Patterned layers have been also performed by synchronizing the movement encoders with the triggering system. In this case we used the acetates based solution of concentration 0.038M. In figure 4, it can be seen a pattern made by independent drops with a pitch of 650µm. The size of the drops is clearly observed and show the high wettability of the substrate by the solution. The thickness in this case is in the range of 50nm, six times thinner than in the case shown in figure 1 where the overlapping increases the amount of material for coating in a similar ratio. In order to obtain thicker drops than those in figure 4 it is necessary to increase the concentration of the solution or to increase the surface tension of the solution to diminish the spreading of the individual drops.

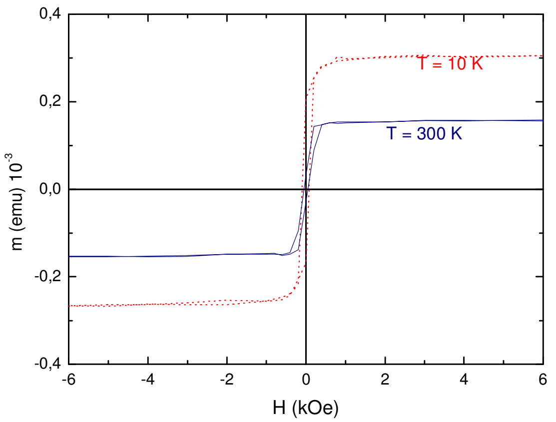

Figure 3. Magnetic moment of the propionates based layer (see text). Magnetization curves have been measured at 300K and 10K

Epitaxially grown lines have been also printed with similar results.

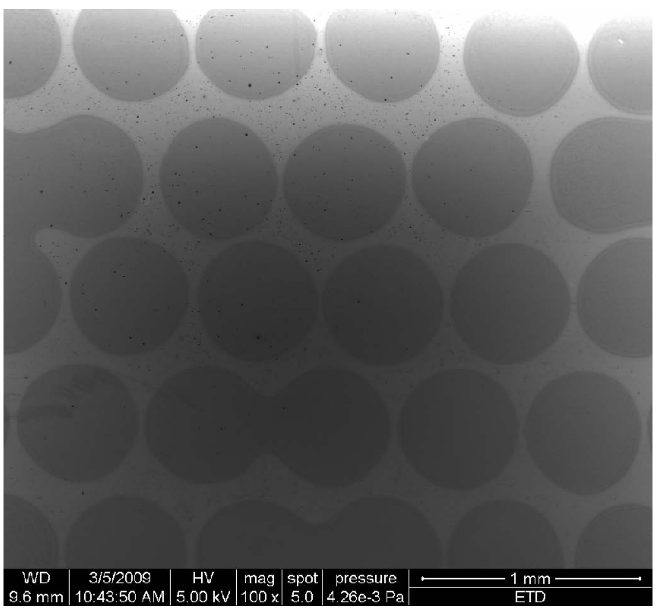

Figure 4 Drop Pattern of LSMO, SEM

Piezoelectric dispenser

The described piezoelectric dispenser has been also to jet ink over LAO substrates with a similar result but with a better capacity to trim the thickness by controlling the drop pitch. In this case, the better pitch for a good overlapping has been experimentally established in 25 µm for 35-40 nL drops. Taken in account the evaporation rate, the distribution of the ink along large areas can be controlled by pining the liquid front with the drops previously placed and partially dried. Due the lower filling speed that in this case can be achieved and the lower volume of the drops, the evaporation rate of solvent acquires a high relevance.

Due to electrical and magnetic properties of LSMO system that are also observable in polycrystalline aggregates, effort to determine its behaviour over lower cost polycrystalline substrates has been paid.

We have used standard alumina substrates of common use in electronics and tracks have been printed over by using LSMO 0.1M ink with rheological correction. Wettability of the alumina substrate was enough to obtain a good layer of ink. After heat treatment at 900ºC in air, the tracks were electrically tested observing electrical conductivity along them in the range of kΩ.

The structure of the LSMO deposition has been observed with SEM being the width of the tracks smaller than 200µm. The layer so obtained show problems of delamination in the parts where the thickness is higher, meanwhile the thinner parts of the track show a good adherence. Figure5 (left) show the tracks with the "peeling" effect. A more detailed insight can be observed in Figure5 (right), the limit of the track can be seen over the grains of Al_2O_3, being some of them half coated. Only over the porous the coating is thick enough to connect the LSMO grains in a sponge-like structure. Conductance testing shows that the tracks are fully connected, however.

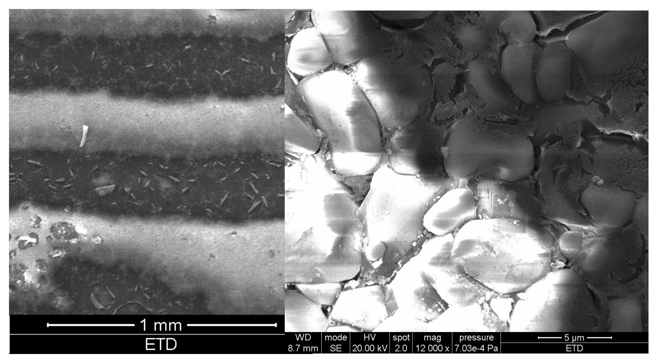

Figure 5 Detail of LSMO printed tracks over commercial alumin. Porosity of alumina produces stress in the thicker regions of the coating producing a peeling effect that can be seen on the left. On the right can be distinguished the behavior on the thin wetted parts clearly opposite to that in the thicker parts where the stress produces dewetting.

Conclusions

The present work shows the feasibility to use CSD precursors used in spin coating technique by adapting their rheology and controlling the solvent, for inkjet printing. Two sets of metal-organic precursors have been adapted for jetting in different conditions and epitaxial grown of LSMO has been achieved in both, full coating and patterned coating. The set of precursor inks can be extended for jetting over polycrystalline substrates but care should be taken with the high roughness of them in order to avoid stress induced dewetting.

The Injk jet technology provides an easy and cheaper way for building electronic devices integrating functional ceramics.

References

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