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Development of relaxor ferroelectric materials for screen-printing on alumina and silicon substrates

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Abstract

The paper describes processing and dielectric properties of $0.65Pb(Mn_{1/3}Nb_{2/3})O_3$-$0.35PbTiO_3$ films deposited on alumina and silicon substrates by screen-printing. Ink development and problems associated with adhesion of electrodes to substrate are discussed in detail. The relative dielectric permittivity, as large as 13,000 have been obtained on SiO_2 substrate after processing optimization.

Keywords: Thick films; Perovskites; Ferroelectric properties

1. Introduction

Relaxor ferroelectrics, like $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$-$xPbTiO_3$ (PMN-PT), are interesting materials for various types of applications. Their high dielectric permittivity[1] is well suited for high capacitance components such as decoupling capacitors. Both relaxor compositions, when correctly biased, and ferroelectric compositions in the vicinity of the morphotropic phase boundary (x around 0.35) exhibit large piezoelectric properties[2,5] that are interesting for high displacement actuators.

In this work, we aim at extending the high potential of these materials to microelectronics and micro-systems applications. One of the main difficulties for these applications is the requirement for low processing temperature (below 900 °C) necessary for a good compatibility with silicon micromachining technology. Screen-printing (for thicknesses above 10 μm) presents a good compromise to obtain materials with properties closer to those of bulk materials than in thin films (<1 μm), and moreover, this process is easily transferable to industrial production. However, treatments at relatively low temperatures often lead to adhesion problems of thick layers (20–40 μm) to smooth substrate surfaces surface.

The relatively low sintering temperatures require development of new inks, compatible with the microelectronics processing in which the maximum temperatures that wafers can withstand is lower than 900 °C. Our previous results show that in the case of bulk samples the maximum of densification for PMN-PT compositions occurs in materials sintered at around 1180 °C for 90 min, leading to samples with very high permittivity.[3] For the same heat treatment, thick films show lower than bulk materials, but still acceptable dielectric and piezoelectric properties when deposited on alumina substrate.[3] Bulk samples sintered at temperatures between 1000 and 1180 °C were not dense and their relative permittivity was low, but the effect was less pronounced for thick films. At sintering temperatures below 900 °C the densification does not occur neither in bulk ceramics nor in thick films when pure micrometer-size powders are used.

The goal of this study is to investigate conditions for obtaining dense films processed at low temperatures. To achieve this goal we first develop inks (active material, volatile and permanent binder), study thermal treatment of the inks and conditions for their deposition. The second step is to improve electrode adhesion to the substrate without using glass additives. These complex processing issues are finally correlated with electrical properties of the obtained layers.

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2. Preparation and properties of films

The screen printable pastes were prepared by kneading ground powders (respectively, 75 and 67.5 wt.%) with organic vehicles (ethylcellulose + α-terpineol). A dispersant was dissolved in several millilitres of MEK (Methyl Ethyl Ketone) before being added to the PMN-PT powder. The MEK was added as a fugitive solvent with the aim of achieving more uniform coating of the PMN-PT powder surfaces by the dispersant.

The effects of starting powder grain size and sintering aid (2 and 4 wt.% with or without PbO addition) and the influence of the substrate (alumina and silicon) and the bottom electrodes (Pt with glass or pure Pt and Au, each sintered at low temperature), on the film quality and properties were investigated.

Two types of PMN-PT powders with different grain size and morphology were used. In one case the powder with the particle size ranging from 0.35 to 1.3 μm with a mean diameter of 0.6 μm, was processed via a modified columbite route.[3] Powders were used pure for optimization of the sintering process on alumina substrate at high temperature and with sintering aids for sintering on silicon wafers. In the other case, the ultra-fine PMN-PT powders, exhibiting grain size from 10 to 100 nm with specific surface areas of 10 to 14 m^2/g, were used. These powders were obtained from sub-micron size powders (specific surface areas of 2.5 m^2/g) by continuous attrition milling in water medium.

After each deposition of the ceramic ink, the care was taken (i) of ink levelling by leaving the substrate on a flat surface at room temperature during 30 min; (ii) of removal of organics, by drying the substrate/film after each deposition at 100 °C for 30 min in an oven; and (iii) of green density, by applying uniaxial pressure on the films.

Samples were annealed under ambient atmosphere. The maximum temperature and dwell time were varied according to the inks composition in order to be compatible with the evaporation kinetic of the different organics. The heating rate was 1 °C/min.

Effect of different sintering aids (Table 1) on densification of screen-printed thick films at lower temperatures was investigated in detail. For these tests, and to avoid cleaving, used substrates were alumina (99.6%) square with double screen-printed Pt bottom electrodes (fired at 1300 °C for 20 min (5–6 μm thick)).

Table 1
List of tested sintering aids with micrometer size PMN-PT powder

Additive	Comment on the film properties
B_2O_3 (2 wt.%)	Good densification but a second phase appears
PbO (4 wt.%)	Film dense enough for electrical measurements but with a large porosity
PbO + B_2O_3	Never gives sufficiently dense films if sintered below 1100 °C
Bi_2O_3-B_2O_3-CdO glass (3 wt.%)	Large amount of second phases
PbO + Bi_2O_3	Large amount of second phases
$Li_2B_4O_7$ (0.7 wt.%)	Good densification with presence of second phases
$LiCO_3$ (2 wt.%)	Best densification and largest increase of the grain size

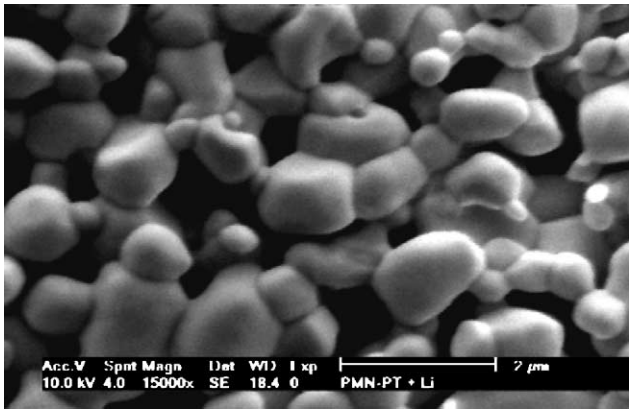

Fig. 1. SEM of thick film surface of 0.65 PMN-0.35PT with Li_2CO_3 (2 °C/min–650°/2 h–3 °C/min–907 °C/5 h).

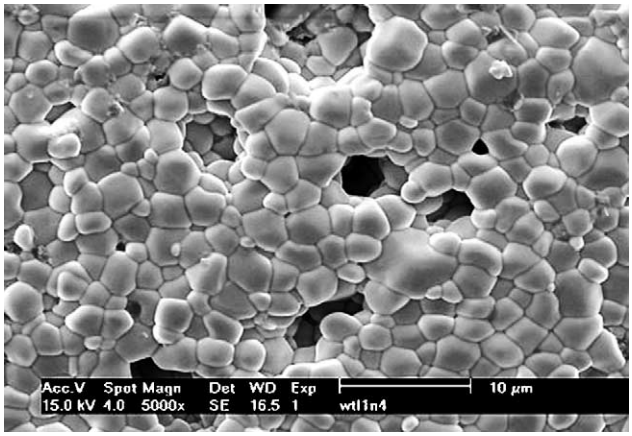

Fig. 2. SEM of thick films surface of ultra-fine 0.65PMN-0.35PT with Li_2CO_3 (2 °C/min–624°/2 h–10 °C/min–880 °C/9 h).

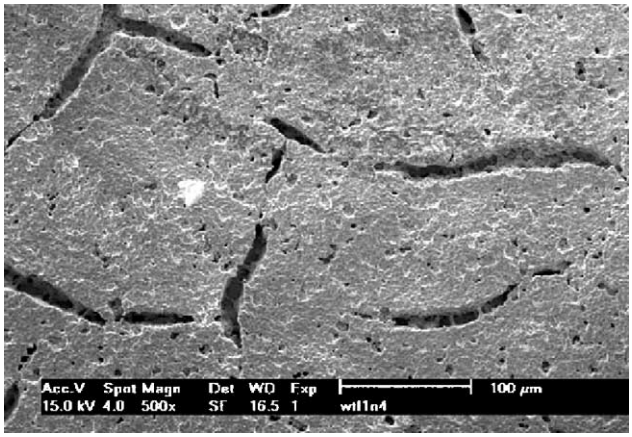

Fig. 3. Cracks in 0.65PMN-0.35PT (ultra-fine powder) films on silicon wafer. Wafer, Si/SiO_2; Electrodes, Pt/Au by screen-printing (2 °C/min–624°/2 h–10 °C/min–880 °C/9h).

Table 2
Effect of adhesion layers and bottom electrode choice on the adhesion of the substrate/electrodes/ceramics layers and the lead diffusion

Different adhesion layers	Pt + glass	Pt/Au
$Ti/TiO_2/Ir$	No diffusion good adhesion	No diffusion low adhesion
Ti/TiO_2	No diffusion good adhesion	No diffusion adhesion
HMDS	Diffusion/reaction good adhesion	No diffusion good adhesion
Ta_5Si_3N	Low diffusion good adhesion	No diffusion large roughness

Thus the best densification and the largest increase of the grain size (Figs. 1 and 2) were obtained at 880 °C with Li_2CO_3 sintering aid added to ultra-fine 0.65PMN-0.35PT powders. However, for the same ink and with the same conditions of deposition and sintering, very large cracks were observed in films deposited on classical silicon wafers (Fig. 3). Those wafers had screen-printed Pt/Au electrodes. The cracking is due to the high thermal strain between the different layers during densification and a bad mechanical adhesion of the bottom electrode onto silicon oxide.

To improve the electrode adhesion onto silicon wafer, we tested (Table 2) influence of substrate roughness on adherence of electrode layers (mechanical adhesion), different adhesion layers such as HMDS (Hexa Methyl di Silazane: $C_6H_{18}Si_2$ which forms strong bond with oxides by silylation) to improve the chemical adhesion, and three different types of electrodes: Pt + glass, Pt/Au, deposited by screen printing and Pt deposited by sputtering. In the case of sputtered Pt bottom electrode, we observed lead diffusion in the silicon oxide layer. This happened even when Pt layer was 300 nm thick.

At the end, the best results were obtained on Si/SiO_2/HMDS/Pt-Au/HMDS substrate, and for the ultra-fine powders of 0.65PMN-0.35PT mixed with the Li_2CO_3. sintering aid.

3. Dielectric results

The best dielectric properties are obtained in films with a grain size between 1.5 and 3 μm. The correlation between the grain size and the permittivity was more pronounced in thick films than in bulk samples[4] or in thin films.[5] The relative dielectric permittivity at room temperature as a function of different sintering parameters is presented in Fig. 4 for thick films deposited on different substrates.

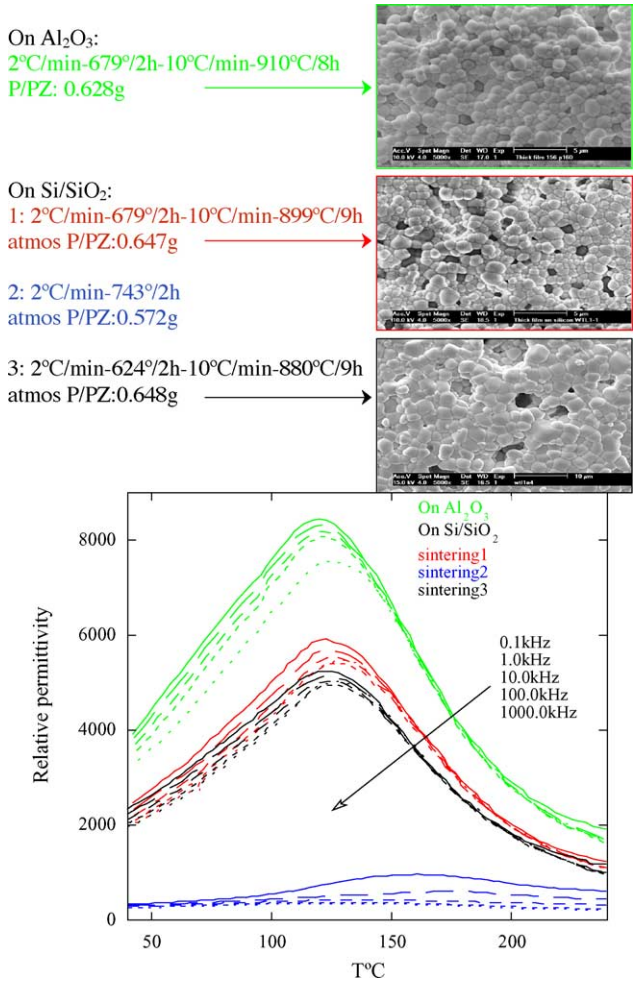

Fig. 4. Comparison of relative permittivity as a function of temperature for thick films prepared from ultra-fine 0.65PMN-0.35PT powder, deposited on alumina and silicon substrates and for different sintering conditions.

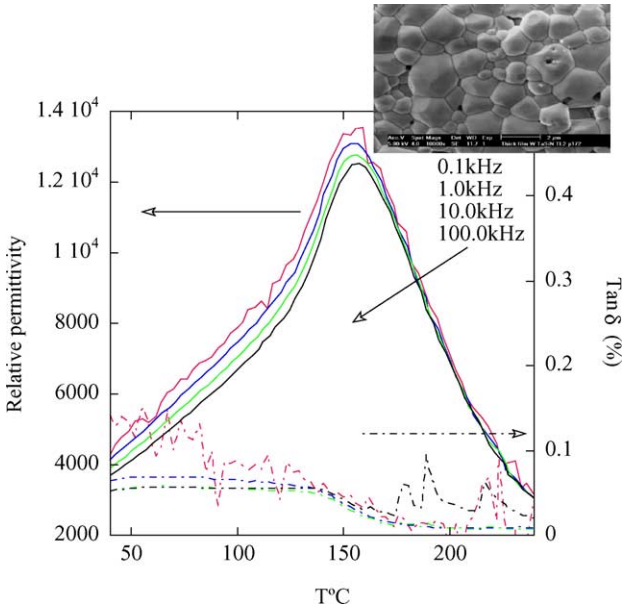

Fig. 5. {0.65PMN-0.35PT ultra-fine powder + Li_2CO_3} ink deposited on Si/SiO_2/HMDS/Pt-Au/HMDS substrate (3 °/min-576 °C/4 h–6°/min-864 °C/10 h).

The lower maximum permittivity in the thick films (6000 on silicon and 8200 on alumina at 1 kHz) with respect to bulk ceramics (16,800 at 1 kHz), may result from several effects, including a larger porosity of the films (density ≈ 92%), films clamping by the substrate, films roughness, presence of a second phase or low-dielectric constant layer between the film and bottom electrode that are not detected by the XRD measurements, and significant lead evaporation due to a larger surface area/thickness ratio in the films than in the bulk samples.

By using HMDS additive layer, film densification was increased and number of cracks was decreased. The dielectric properties were consequently improved as shown in Fig. 5. In this case the samples with the relative permittivity around 13,000 at its maximum (at 1 kHz) were obtained, compared with 6000 in samples prepared without adhesion layers. The dielectric losses in these samples were relatively low at all temperatures (2%).

4 Conclusion

First dense (94%) 0.65PMN-0.35PT thick films on silicon wafer were prepared by using ultra-fine powders and Li_2CO_3 additive. The maximum of relative permittivity of 0.65PMN-0.35PT thick films sintered at 890 °C were 8200 and 6000 for films deposited on alumina and silicon substrate, respectively. These values are lower than in bulk ceramics (18,000) prepared at a higher sintering temperature (1190 °C).

Much better results were obtained if an HMDS adhesion layer was used. In that case, the permittivity increases from 6000 to 13,000, while the dielectric losses remain low (2%).

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