Microstructural analysis of TiO_2-$CoFe_2O_4$ film

Pietro Galizia, Davide Gardini, Carlo Baldisserri, Carmen Galassi

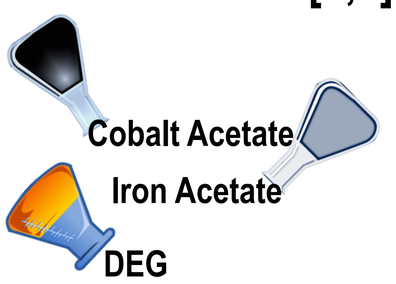
CNR-ISTEC, Via Granarolo, 64, 48018 Faenza (Italy)

Abstract

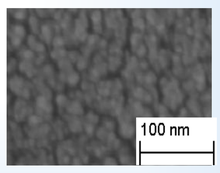
Electrophoretic deposition (EPD) from colloidal suspensions in ethanol was utilized to tailor the microstructure of the composite magneto-dielectric films. The deposition was made from a colloidal suspension keeping constant voltage and recording the current. Good adhesion and compaction of the green film were achieved by optimization of deposition voltage and time while high density of the film and minimized interphase reactions occurred after sintering. The deposited volume, the mixing of dielectric and magnetic phases and the density and ordering of the films have been verified by electron scanning microscopy before and after heat treatment.

Suspensions

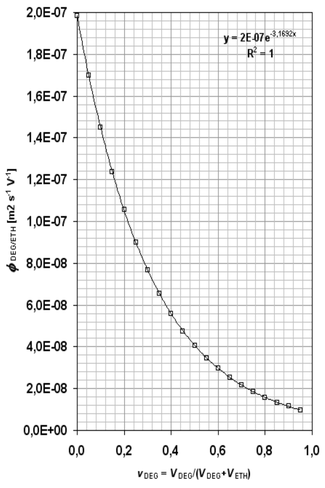
1 - Cobalt Ferrite [1,2]



Stoichiometry (spinel) :	$CoFe_2O_4$	
Particles Density:	5.27	g cm^{-3}
Suspension Density:	1.23	g cm^{-3}
Solid Loading, wt%:	12.9	
Particle Size (DLS):	10.1	nm
Viscosity:	56.7	mPa s
ζ-potential :	47.5	mV
Electrical Conductivity:	15	µS cm^{-1}



- Solubilisation at 110°C for 1 h
- Heating to 180°C (2°C/min)
- 3h at 180°C
- Air cooling to RT

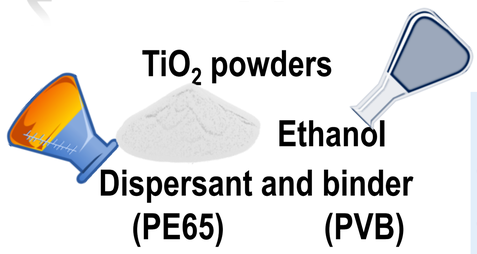


Dilution with ethanol [3]

Reduced viscosity of the mixed DEG/ethanol medium increase particle flux by increasing the mobility per unit ζ-potential (figure of merit, Φ) and give beneficial effects on film coagulation.

$$\mu = \frac{2}{3}\frac{\zeta\varepsilon}{\eta} \qquad \phi = \frac{\varepsilon}{\eta} = \frac{3\mu}{2\zeta}$$

2 - Titania [4]



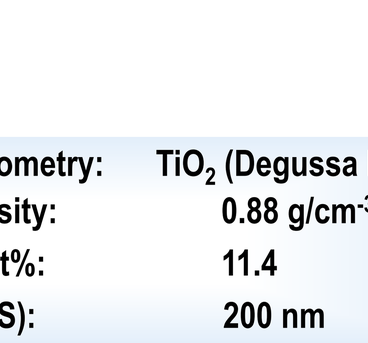
Particles Stoichiometry:	TiO_2 (Degussa P25)	
Suspension Density:	0.88	g/cm^{-3}
Solid Loading, wt%:	11.4	
Particle Size (DLS):	200	nm

- Ball milling and stirring

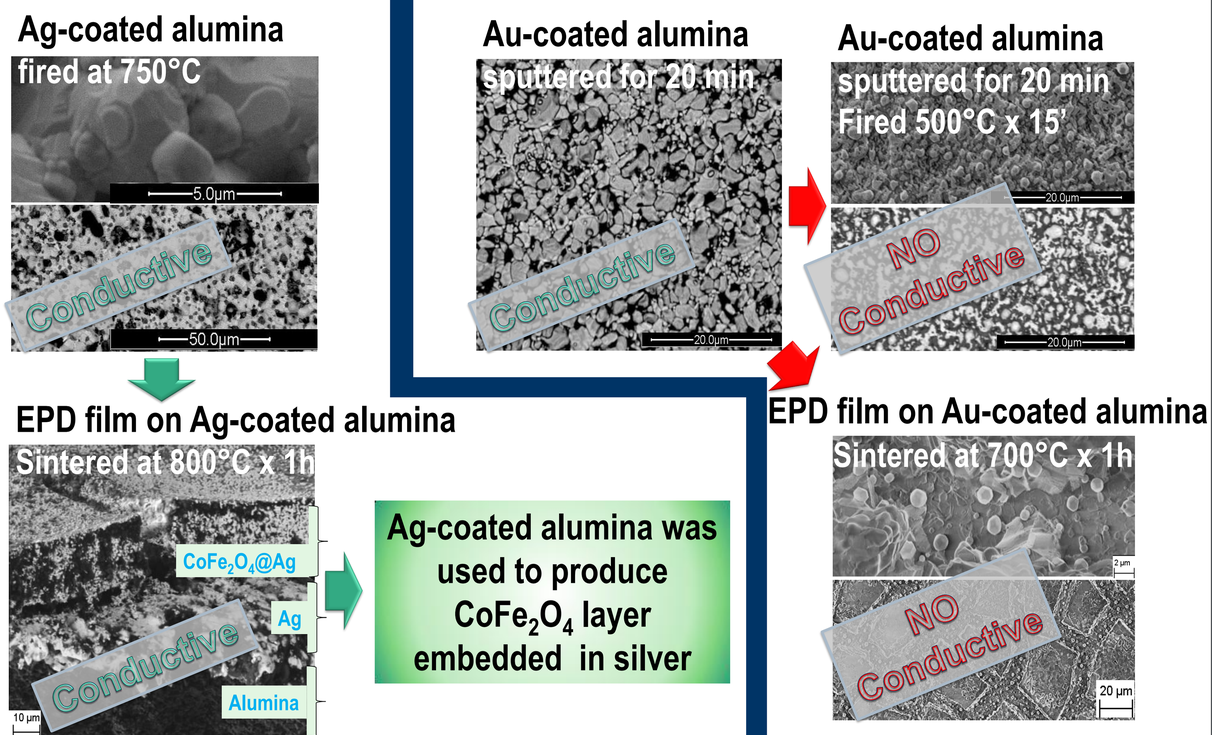
3 - Lead zirconate titanate [5,6]

Particles Stoichiometry:	$Pb_{0.988}(Zr_{0.52}Ti_{0.48})_{0.976}Nb_{0.024}O_3$
Suspension Density:	0.88 g/cm^{-3}
Solid Loading, wt%:	11.3
Particle Size (DLS):	1075 nm

- Ball milling and stirring



Conductive substrate

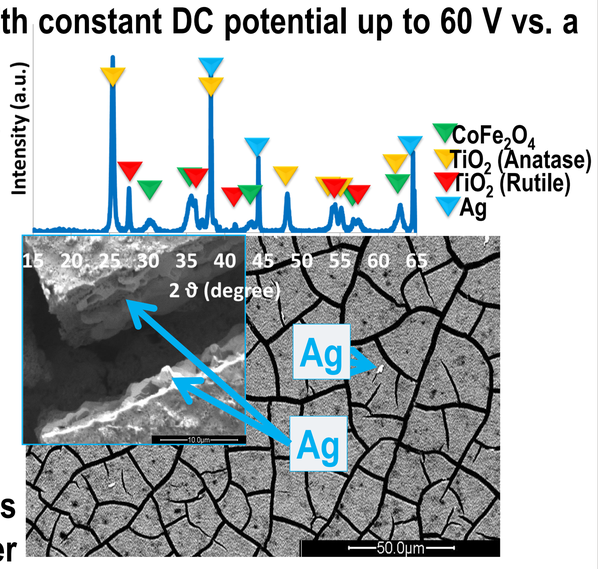


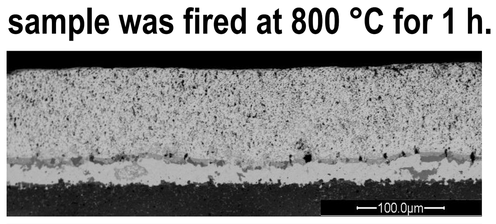
Process

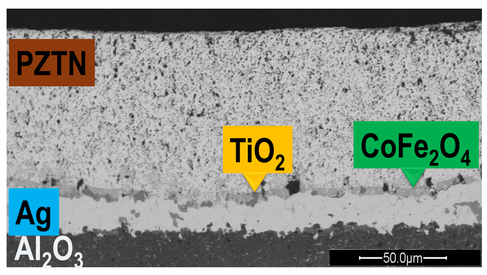
EPD tests were performed in a plane-parallel cell geometry (1 cm electrodes spacing) and setting cathodic modality with constant DC potential up to 60 V vs. a 20 cm^2 SS secondary electrode.

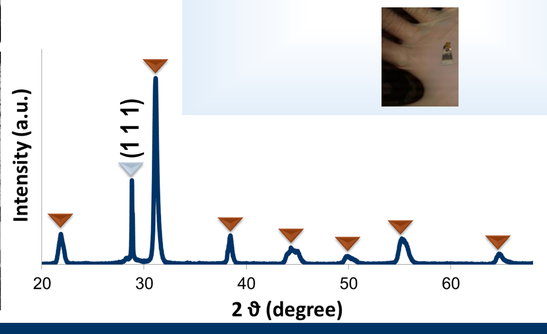
<u>First layer</u>: a suspension obtained by mixing the Cobalt Ferrite suspension with the titania one was deposited. CFO/TiO_2 weight ratio of suspension, voltage and time deposition were 4, 50 V, 100 sec, respectively. After drying in ethanol rich atmosphere, the sample was fired at 500 °C for 15 min.

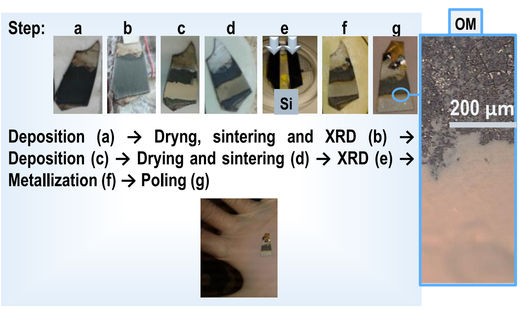
<u>Second layer</u>: PZTN suspension was deposited under 30 V for 50 sec. After drying in ethanol reach atmosphere, the sample was fired at 800 °C for 1 h.







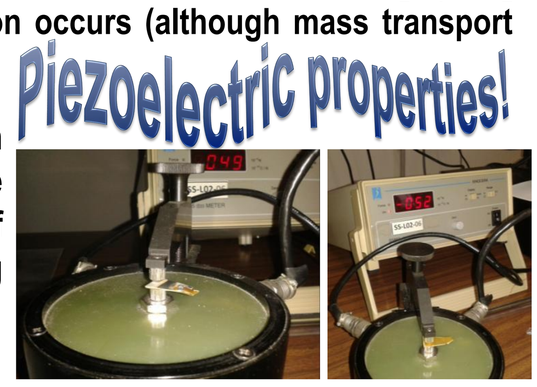




Conclusions

Magnetoelectric thick film on Ag-coated alumina was produced.
The microstructure analysis was performed by SEM/EDS and XRD.
A 70-100 sec minimum deposition time is required to deposit $CoFe_2O_4/TiO_2$ suspensions, otherwise no film coagulation occurs (although mass transport takes place).

Although cracking occurs during drying in air, a pre-sintering heat treatment in the range of 400-500 °C gives a good stability of the $CoFe_2O_4/TiO_2$ film and allows the Ag wetting of the cracks.



References

[1] G. Baldi et al., J. Magn Magn Mater 311 (2007) 10-16
[2] D. Gardini et al., J Nanosci Nanotechnol 8 (2008) 1979-1988
[3] C. Baldisserri et al. Key Eng Mat, 507 (2012) 85-88
[4] C. Baldisserri et al. J Colloid Interface Sci, 347 (2010) 102–111
[5] C. Baldisserri et al. Sensor Actuat A-Phys 174 (2012) 123-132
[6] C. Galassi et al. J Eur Ceram Soc, 17 (1997) 367–371

Contact author: pietro.galizia@istec.cnr.it (Pietro)