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Numerical models for describing dielectric and ferroelectric properties in composites systems

A thesis submitted by

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I. Introduction

I.1 Ferroelectricity

Ferroelectric materials are o subclass of dielectric materials and are characterized by a nonlinear dependence of the polarization *vs.* applied electric field which can be hysteretic below a critical temperature called Curie temperature (T_C) [1].

The main properties of ferroelectric materials are [2,3]:

- Ferroelectrics are characterized by a domain structure below T_C, each domain being characterized by a spontaneous polarization P_s. The dependence of the macroscopic polarization on the applied field is hysteretic. Above T_C, the domains structure vanishes and the $P(E)$ dependence becomes non-hysteretic, but remains nonlinear. The effective permittivity is modifiable by changing the applied field, property called ”tunability”. Mathematically, the tunability is defined as the ratio between permittivity at zero field and permittivity at an applied field E: $n = \varepsilon(0)/\varepsilon(E)$. The $\varepsilon(E)$ dependence is also hysteretic below T_C and non-hysteretic above T_C.
- Ferroelectric materials are characterized by a first or a second order phase transition when they pass from their polar (ferroelectric) state to the non-polar (paraelectric) state. The non-polar state is always characterized by a high crystalline symmetry than the polar state.
- The temperature dependences of the electrical, mechanical, optical and thermal properties present anomalies around the Curie temperature.

I.2 Applications of ferroelectric materials

Due to their large number of interesting functional properties, ferroelectrics are used in a wide range of applications in electronics, from simple passive elements of circuit like capacitors, to complicated devices in microwaves, with active functions.

Ferroelectric materials like *PZT*, *BT* and their based solid solutions present huge dielectric constant (from 10^3 to 10^4) in a large range of frequencies. This property has imposed ferroelectric materials as the best candidates for Multi-Layer Ceramic Capacitors (MLCC) (Fig. I.7). A MLCC can be described as a group of microcapacitors with interdigitated electrodes connected in parallel. A microcapacitor corresponds to the ceramic region between two successive electrodes and has a high capacitance due to the small thickness.

Due to the polarization reversal and to their hysteretic properties, ferroelectrics are used below T_C as non-volatile Ferroelectric Random Access

Memory (FeRAM) [4]. The "up" or "down" polarization represent the computational 0 or 1 bit of memory.

Other types of applications in RF and microwaves use the tunability properties of ferroelectric materials. Therefore, ferroelectrics have been proposed in developing various devices as: oscillators, phase shifters, varactors etc, lens antennas [5].

Other applications use the piezoelectric, pyroelectric and electrooptic properties of ferroelectrics: transducers, medical imaging, telecommunications, ultrasonic devices, modulator switches etc.

I.3 A few open problems. Motivation of the present study

In the last decades, new research directions have been opened in material science in order to accomplish specific applications requirements. Although the number of applications is large, we can state that nowadays all the microelectronics applications are characterized by the same major requirement: the need for *miniaturizations*. The main objective of this thesis was to propose a modeling approach to design optimum ferroelectric-based composite structures for a few specific applications, in which their enhanced permittivity, tunability and switching responses to be exploited.

In the following we will summarize a few actual problems concerning ferroelectric materials, that will be approached from theoretical point of view in the present thesis:

1) Grain size effects in ferroelectrics. In order to increase the capacity MLCCs, the best solution is to reduce the thickness of microcapcitors. In the last years, this thickness has got to 0.5 µm, which imposed the necessity of developing ceramics with grain sizes (GS) below 100 nm. Therefore, the study of the grain size effect on the functional properties has become of great importance in the last years. [6,7].
2) Ferroelectrics for tunability applications. The requirements in tunability applications are: large tunability (>1.5), moderate permittivity (<1000) and low losses [5]. The most of the single phase ferroelectrics are characterized by high permittivity and, for this reason, ferroelectric-based composites with a linear dielectric phase have been proposed. Unfortunately, the reports in literature proved that, when the microstructure is not controlled, both permittivity and tunability are reduced with increasing the dielectric phase concentration. A challenge for material scientist is to find ways to keep the tunability high when reducing the effective permittivity.
3) Ferroelectrics for energy storage application. Ferroelectrics present a great potential for energy storage applications due to their huge dielectric constant. However, for this type of applications the tunability is undesired because it

reduces the capacity of storing energy at high fields. A modern challenge for material scientist is to find ways to reduce tunability while keeping the permittivity high.

4) Nonlinear dielectric properties in flexible electronics. A special class of polar dielectrics that present tunability properties is represented by polymers like poly vinylidene fluoride (*PVDF*). These materials can be used in flexible electronics. By comparisons with ferroelectric ceramics, polymers are characterized by much lower permittivity (few units) and much lower tunability. Therefore, it is necessary to find ways to increase tunability of such materials.
5) Nanoscale ferroelectric memories. Another actual challenge for ferroelectric materials derived from the need of miniaturization, is related to the production of memories with increased storage capacity. In order to reach density as high as 1Tb/inch^2, memory devices containing nanocapacitors are required. Recently, some new experiments [8,9], showed that in case of PZT-based memories in configuration of nanocapacitors with the radius of 35 nm, the writing process of one bit affects the neighboring bits of memory. This phenomenon is called "cross-talk" and is undesired because it is a limitation for increasing the memory density. An actual problem is to find ways to avoid this phenomenon in memories at nanoscale.

II. Numerical models for describing ferroelectric properties

II.1 Introduction

In the last years, a large number of numerical models were proposed for describing functional properties of ferroelectric materials at different length scale: *ab initio* model at elementary cell level, *Landau* theory and *Monte Carlo (MC)* models at microscopic level, *Preisach* model and *Finite Element Method (FEM)* at macroscopic level. The novelty of the thesis is the combination of FEM with other models for describing the role of some peculiar microstructures on the functional properties. The models used in simulations will be presented in the following.

II.2 Landau theory

The Landau theory was employed to describe nonlinear dielectric properties of ferroelectrics in paraelectric state. The Johnson's equation [10], derived from Landau theory, was used to describe locally the dependence of the local permittivity on the local electric field in ferroelectric based composites.

II.3 Monte Carlo models

MC models (like Ising model [11]), describe the switching processes of ferroelectrics at a level comparable to the size of domains. This model was used to describe the "cross-talk" phenomenon in ferroelectric nanocapacitors arrays.

II.4 Preisach model

In Preisach model a ferroelectric system is considered a being composed from microscopic hysteretic be-stable units called *hysterons* which are characterized by different coercive fields [12]. Therefore, this model is more appropriate to describe switching processes in large scale ferroelectrics like ceramics. The Preisach model was used to describe switching processes in porus *PZTN* ceramics.

II.5 Finite Element Method

FEM was employed to describe the inhomogeneity of the local electric field in composites or ferroelectrics with specific boundary conditions [13-18]. FEM was combined with Landau theory for describing nonlinear dielectric properties of ferroelectric-based composites, with Preisach model for describing switching phenomena of porous ferroelectrics ceramics and with MC models for describing the "cross-talk" phenomenon in ferroelectric nanocapacitors arrays.

III. Non-linear dielectric properties of ferroelectric-based composites

III.1 Introduction

In Chapter III, we have investigated the role of the microstructural features in various ferroelectric/dielectric composites on their nonlinear dielectric properties. For these kind of studies, we have developed a special procedure in which the Laplace equation was solved by considering a Johnson non-linear dependence of the local permittivity upon the local electric fields for the ferroelectric component. The selected microstructural configurations of the di-phase composites were chosen in order to cover the main types of composites proposed in practical situations. The main conclusions derived from our simulations are detailed below, for each type of investigated configurations.

III.2 Composites with randomly distributed phases

The effective permittivity is reduced and tunability can be enhanced by decreasing the permittivity of the dielectric phase. Therefore, among all the possible combinations of ferroelectrics with low permittivity phases, the **porous ferroelectric materials** ($\varepsilon_{lin} = 1$) present the lowest permittivity and the highest tunability, at a given field, due to the huge contrast in the parent phase permittivity, which produce a high perturbation of the local field lines. Although porosity was usually considered undesired in electroceramics applications, our calculations clearly showed that a small amount of porosity may be beneficial for enhancing non-linear dielectric character, by comparison with ones of the dense materials, while reducing permittivity to values of hundreds.

For a given combination of ferroelectric and dielectric parent phases, both the effective permittivity and tunability are reduced when increasing the concentration of the linear dielectric phase. Therefore, the combination of such high/low permittivity parent phases without any microstructure control (*e.g.* by simple mixing, which usually provides a randomly distributed phases) will always result not only in a decrease of permittivity, but also of tunability response.

III.3 Composites with ferroelectric inclusions (0-3 connectivity)

The effective permittivity is close to the permittivity of the low-permittivity phase and the tunability is reduced to zero for this configuration, due to the fact that the field on the ferroelectric component is almost completely suppressed. Therefore, in any kind of combination of ferroelectrics embedded in a low-permittivity matrix, the dielectric response is dominated by the low-permittivity phase. The results of these calculations demonstrate that it is impossible to enhance permittivity and to induce a non-linear dielectric response and ferroelectric switching in polymer-based composites by the addition of a high-permittivity phase. However, this configuration is interesting for energy storage applications because permittivity remains field-independent up to very high field values. By a proper choice of the two phases, optimum combinations for energy storage can be designed (as for example, composites formed by inclusions of BZT or other BT-based solid solution with a high permittivity into a ST matrix). Ferroelectric nanostructured ceramics are a particular case of the general type of composites with ferroelectric inclusions (grain core) into a linear dielectric matrix (low-permittivity grain boundary). We employed our approach to explain the role of grain size reduction on the dielectric and tunability properties of nanostructured $BaTiO_3$ ceramics with GSs in the range from 5 μm to 100 nm. The FEM calculations showed that the effective permittivity and tunability are reduced when decreasing grain size, while $\varepsilon_r(E)$ dependence is modified from a Johnson-like dependence to a remarkable linear one.

III.4 Composites with 0-3 connectivity and ferroelectric matrix

This configuration was analyzed in two cases: low permittivity linear inclusions ($\varepsilon_{lin} = 10$) and infinite permittivity (conductive) inclusions.

If the low permittivity inclusions are fully isolated into the high permittivity ferroelectric matrix (0-3 connectivity), the simulations show that the effective permittivity continuously reduces when increasing the filling factor of the dielectric phase, while the tunability maintains its values close to ones of the ferroelectric single phase. This result allows proposing designed combinations of materials with expected high tunability and permittivity of a few hundreds, required for tunability applications.

If the inclusions are characterized by higher permittivity than the permittivity of the matrix, both effective permittivity and tunability are strongly enhanced, by increasing the concentration of the inclusions. This result might be useful when the matrix is a polymer, which has usually too low permittivity (usually of a few units) for being employed as active dielectric material in microelectronics. Based on this configuration, composites with high permittivity dielectrics (or conductive) inclusions into a nonlinear polymer matrix can be designed, for flexible electronics applications. We checked the model predictions for a composite with Chitosan matrix filled Gold nanoparticles for which an increase of tunability form 2.0 to 2.3 with increasing the Gold concentration form 0% to 2.5 % was observed.

III.5 Composites with columnar dielectric inclusions into a ferroelectric matrix (1-3 connectivity)

This configuration presents anisotropy and was analyzed in two cases: inclusions orientated parallel to the applied field direction and inclusions orientated perpendicular to the applied field direction.

In the case of elongated inclusions oriented with their long axis parallel to the applied field direction, the effective permittivity presents a linear decrease with increasing the content of the linear dielectric phase, while the tunability remains almost unchanged. For a certain concentration of the linear dielectric phase, the permittivity in this configuration is the highest by comparison with all the other configurations.

When the inclusions have their long axis perpendicular to the direction of the applied field, the effective permittivity presents a strong reduction with increasing the concentration of the dielectric phase, which is comparable with the permittivity decrease in composites with randomly distributed phases. However, the tunability is remarkable higher than the tunability of the single phase, even for a high content of the dielectric phase (up to 50%). Therefore, this configuration showed the most promising premises for tunability applications than all the other configurations studied in this thesis and is strongly recommended to the experimentalists for being produced. Even the 1-3 phase assemblage is quite difficult to be realized by traditional processing, the calculations shows a very promising potential tunability and such structures should be tried to be produced by unconventional or combined methods. In this case, an additional parameter to control the effective permittivity is the anisotropy of inclusions: higher permittivity for inclusions oriented along the applied field direction and lower permittivity for inclusions oriented perpendicular to the direction of the applied field. The idea of anisotropic permittivity and tunability was experimentally confirmed for anisotropic *PZTN* ceramics with elongated pores, which even not fully controlled as 1-3 connectivity, shows very clear trends, similar with the computed ones.

IV. Modeling of switching phenomena in specific ferroelectric micro- and nanostructures

IV.1 Introduction

In this chapter, the switching phenomena in some specific micro- and nanostructures have been investigated. In order to take into consideration the local field modifications induced by the presence of interfaces between di-similar materials, again FEM calculations have been employed. Further, the resulted local field distributions have been considered in calculations as input for the switching models. The main results for a few structures are described below.

IV.2 Switching in porous ferroelectric ceramics

In order to describe the role of porosity on the switching properties, we have proposed a complex approach in which Preisach model was applied locally for small elements, after estimating the local fields by the FEM procedure. This approach succeed to reproduce the main experimental trends induced by the increase of porosity on the switching properties: a nonlinear reduction of the saturation/remanent polarization, the modification of the hysteresis loop shape from rectangular to a tilted one [19] and modifications of the FORC distributions towards broader distributions.

IV.3 Cross-talk phenomena in ferroelectric nanocapacitor arrays

The switching of individual elements in nanocapacitor arrays is considered as a very promising way to increase the storage capacity towards 1Tb/inch^2, but experiments showed the presence of undesired cross-talk phenomena. This part of our study was dedicated to explain the switching dynamics in such systems, for various experimentally accessible parameters, in order to provide some solutions to avoid such phenomena and to optimize the nanocapacitor arrays nanostructures. The local fields have been computed by using 3D FEM calculations and the switching properties under the local fields have been determined within a Monte Carlo model [20]. The results of this approach explains the appearance of cross-talk phenomena as a consequence of the evolution of local dipoles under the local electric fields and considering their reciprocal interactions.

After understanding the reasons for the appearance of this phenomenon, a few solutions to avoid it have been proposed: the increase of the distance between nanoelectrodes, the reduction of the applied voltage and the reduction of the ferroelectric film thickness down to a few nanometers. Among the proposed solutions, the reduction of the film thickness is the most effective one, because in this case the local electric fields under the neighboring electrodes are strongly reduced and the central domain remains confined under the central electrode. Additionally, the speed of the writing process is much improved, due to the enhancement of the local field under the central electrode.

V. Conclusions

In all the investigated systems the local electric fields inhomogeneity, introduced either by interfaces between different phases or by particular boundary conditions, prove to play a crucial role on the functional properties. Therefore, the major conclusion of this research is that functional properties of ferroelectric-based systems can be tailored by local field engineering, trough controlling their microstructural features. The solution of improving properties by material design based on modeling in combining di-similar materials in composites to reach peculiar microstructural parameters, which can be realized by advanced chemistry, should replace the large-scale trial-and-error methods of mixing materials.

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The original results have been materialized in 7 ISI articles (19 citations), 46 presentations at international conferences (22 oral presentations), 4 international prizes and participations as member in 5 national projects and 2 international projects. The scientific activity is presented in attached annexes at the end of the thesis.

Total influence score: 6.765
Total impact factor: 17.656
Individual ISI score: 4.094