



Chemical segregation and self polarisation in ferroelectrics

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Abstract

Chemical partitioning or segregation is commonly encountered in solid-state syntheses. It is driven by compositional, thermal and electric field gradients. These phenomena can be quite extreme in thin films and lead to notable effects on the electrical properties of ferroelectrics. The segregation in ferroelectric thin films will be illustrated and the mechanisms explained in terms of diffusion processes driven by a potential gradient of the oxygen. The hypothesis can also explain self polarisation and imprint in ferroelectric hysteresis.

Keywords: ferroelectric, segregation, diffusion, self-polarization, kinetic demixing

I. Introduction

Ferroelectric thin films ($< 1 \mu\text{m}$) have been studied intensively over the last 20 years and the corresponding technology has advanced considerably. Both vacuum (sputtering, pulsed laser ablation deposition) and chemical (sol gel, metal organic vapour phase deposition) techniques have been used to fabricate oxide films. However, chemical solution methods are low cost easily accessible routes that have made it possible for many researchers to carry out studies in this field. A characteristic of these methods is also the complex chemistry involved both in the preparation of the solutions as well as during the thermal processing needed to pyrolyse the organic ligands and, eventually, crystallise the oxide. Development of thin films technology has led to the fabrication of numerous microelectronic devices such as memories, sensors and micro-electromechanical systems, with improved ferroelectric, pyroelectric or piezoelectric properties. This research also led to a renewed interest into the nature of ferroelectricity and, particularly, the behaviour of ferroelectrics on a submicronic scale. The chemistry and metallurgy of the interfaces between the ferroelectric film and both the substrate and top surface including the interaction with environment play a much greater role. Consequently, the electrical properties are strongly influenced by surface reactions and interdiffusion that takes place during the fabrication of the film.

This paper discusses some of the segregation phenomena observed on ferroelectric oxide films. Sol gel methods used to prepare both $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) and $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) are illustrated and the correlation between the synthesis and segregation is explained; practical indications on how improvements could be made to optimising the ferroelectric properties of these materials are presented.

II. Film preparation

2.1. Preparation of $\text{Pb}(\text{Zr,Ti})\text{O}_3$ sols

PZT films are the most investigated ferroelectrics and so many syntheses have been developed, but we used a method developed by Dey and Payne [1] that has been particularly successful.

The scheme in Fig. 1 shows the synthesis of the precursor solution using lead acetate, titanium isopropoxide, zirconium propoxide and methoxyethanol. The solutions are made following a certain procedure. This involves an accurate control of the distillation temperatures to avoid pyrolysis and reduction of the organometallic species. The temperature of the distillation must be kept low by vacuum distillation and not allowing the solution to become overheated in contact with the flask walls. The reactions involve the removal of water from the lead acetate trihydrate, followed by reaction of the lead acetate with methoxyethanol. The zirconium and titanium propoxides were converted to their respective methoxyethoxides by distillation and added to the previously prepared lead acetate solution. Three further distillations and dilutions were performed to leave

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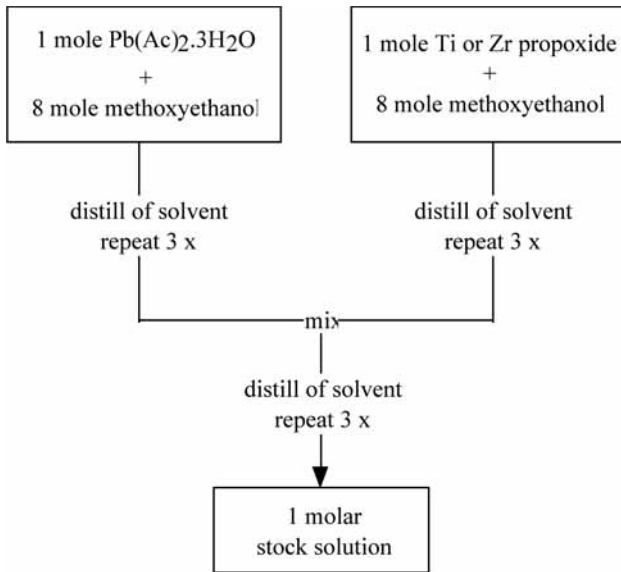


Figure 1. Flow diagram illustrating the synthesis of precursor solutions for the deposition of PZT films

a 1 M solution containing the stoichiometric amounts of Pb, Zr and Ti to produce $\text{Pb}_{1.1}\text{Zr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ films. Lead was added in 10% excess to aid crystallisation of the perovskite phase.

This is followed by hydrolysis, which creates a sol by substitution of the alkoxide ligands by hydroxyl groups. This step can also be used to control the temperature at which ligands are eliminated once the sol has been deposited onto the substrate. The hydrolysis was performed by adding a solution of water 1 M in methoxyethanol dropwise with stirring to an equal volume of water 1 M in methoxyethanol.

2.2. Preparation of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ sols

Strontium acetate, dissolved in acetic acid, was added to a solution of bismuth ethylhexanoate and tantalum ethoxide in ethylhexanoic acid, stabilised with methoxyethanol and diethanolamine. Again care must be taken in preparing the precursors, particularly the bismuth ethylhexanoate, which is made by reacting bismuth acetate with ethylhexanoic acid. The bismuth ethylhexanoate is prone to pyrolysis if the distillation temperature is too high resulting in a darkening and precipitation of metallic Bi. The distillation temperature kept at approximately 100°C, however, the elimination of acetic acid is controlled principally by per-

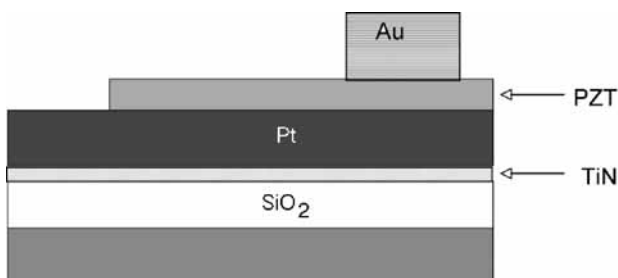


Figure 2. Typical ferroelectric capacitor stack used to measure the dielectric properties of ferroelectric films

forming the distillation at pressures below 100 mbar, using a chemical vacuum pump. Moreover, the product is quite viscous and stirring is carried out using a mechanical paddle to clear the ensure that the reactants are not in prolonged contact with the heat source. The techniques used are described by Watts et al. [2].

2.3 Film deposition

Films are normally deposited on platinised silicon substrates to create a capacitor stack as illustrated in Fig. 2. This is a typical structure showing the oxidised silicon substrate, a TiN adhesion layer for the bottom platinum electrode, the ferroelectric deposited one or more sequences and a top electrode, in this case gold.

The oxide film crystallises after heat treatments at various temperatures, generally carried out in two steps:

- Low temperature pyrolyses (200–400°C) are performed to remove solvents and organic ligands, leaving a nano-crystalline or amorphous.
- At higher temperatures (500–800°C) to crystallise the ferroelectric and optimise its dielectric properties.

2.4 Film characterization

The electrical properties of the films were measured using a HP 4284A LCR meter for the C-V measurements and a home built Sawyer and Tower circuit for the P-E hysteresis measurement. The concentration profiles of SBT and PZT films were analysed by Secondary Ion Mass spectroscopy and X ray photoelectron spectroscopy, respectively. The details of the experiments have been described previously [3,4].

III. Results

A complete structural and electrical characterisation of the films has been performed previously [5–7]. These works show that suppressing the diffusion of Ti from the adhesion layer, using TiN between the Pt and SiO_2 , gave films with stronger ferroelectric hysteresis and eliminated spurious phases, particularly, in the case of SBT.

The SIMS concentration profile of the SBT film is shown in Fig. 3. Although the curves do not plot absolute values of concentration the variation versus depth into the film is quite well illustrated. The profiles were measured from the surface of the SBT film, through the Pt electrode and into the TiN adhesion layer. One can see that the concentrations are hardly homogeneous in all three layers but there has been a great degree of interdiffusion. Bismuth is the element that has diffused mostly, enriching the surface over a distance of 20 nm, and into the TiN adhesion layer. The surface enrichment is accompanied by depletion in the region immediately below the surface.

Fig. 4 shows a profile of the PZT film measured using by XPS at different depths after sputtering. In this case only a surface enrichment is observed. Although

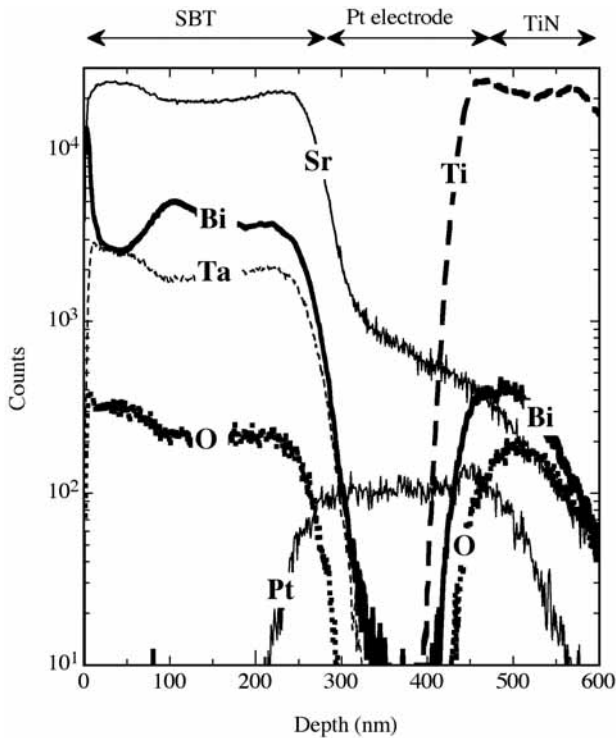


Figure 3. Concentration profiles of a $\text{SrBi}_2\text{Ta}_2\text{O}_9$ film determined using SIMS [3]

this has been observed in many studies it has often been dismissed as an artefact of the analytical technique. XPS analysis of a lapped surface of PZT ceramic indicated that sputtering barely altered the surface composition hence the enrichment is a real effect [4,8,9]. Moreover, the comparison of the oxidation state of lead in the film and in the ceramic indicates that there is a marked contribution from the Pb^0 relative to the Pb^{IV} peak in the Pb 4f spectrum in the PZT. Sputtering can reduce the lead but an analysis of the PZT ceramic suggested that most of the reduction of the lead occurs during the preparation by sol gel technique. Thus, the pyrolysis step needs to be performed carefully so that the organic ligands are combusted

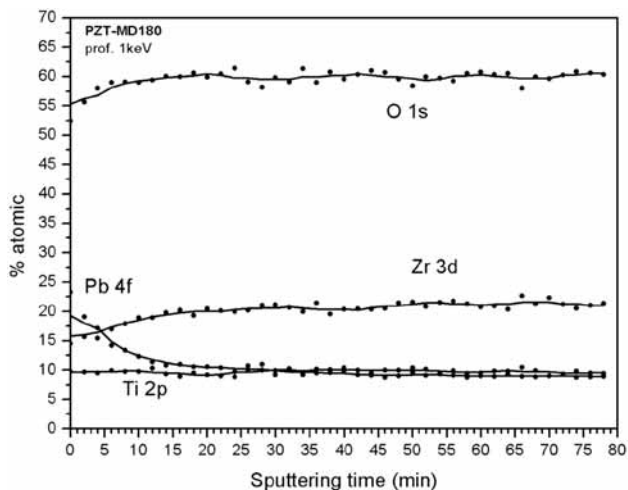


Figure 4. Concentration profiles of a PZT film determined using XPS [4]

fully; this can be done by slowly heating to the pyrolysis temperature, depositing thinner layers, increasing the degree of hydrolysis or carrying it out under highly oxidising conditions [10].

IV. Discussion

4.1 Diffusion into bottom electrode

Fig. 3 shows that severe diffusion into the bottom electrode takes place. Bismuth is found in the TiN buffer layer. Similar effects have been observed for PZT films [11]. It is worth noting that the concentration of Bi is low in the Pt and it appears that driving force for diffusion is the reaction between bismuth, titanium and oxygen, most probably to form a stable compound such as $\text{Bi}_4\text{Ti}_3\text{O}_{12}$.

Studies have shown that the buffer layer influences the properties of PZT and SBT [12] and improvements are obtained if this layer has a limited reactivity with the lead or bismuth. Thus, one would expect CeO_2 or IrO_2 to lead to improvements in ferroelectric devices.

Metals, such as lead and bismuth, react with or dissolve in platinum [13]. Ensuring that no metallic lead or bismuth is present in the sol gel film can lower the diffusion of these metals into the bottom electrode. The syntheses of the film were described above and it can be seen that every stage (precursor synthesis, sol preparation and film deposition) has influence on the degree of oxidation of the ferroelectric oxide that crystallises [3,10].

4.2 Diffusion to the surface

Historically, ferroelectric oxides have been prepared as bulk ceramics, by high temperature sintering, typically at 1200°C . Under these conditions the lead evaporates thus the green ceramic is normally packed inside lead zirconate powder, to create a lead rich atmosphere around it. Thus, it was assumed that the mechanism that caused Pb and Bi losses near the surface of films was evaporation. Figs. 3 and 4 show that there is, in fact, surface enrichment and the depletion layer is a subsurface region from where these metals have diffused. Sometimes, the driving force is attributed to the PbO and Bi_2O_3 lowering the surface energy. However, this seems insufficient and does not offer a complete understanding of how the phenomenon can be reduced.

An analogy may be drawn with the oxidation of metals such as Cu and Sn, where the metals diffuse towards the reacting surface, as described by Cabrera and Mott [14] and Wagner [15]. The data presented here indicate that the pyrolysis and crystallisation steps result in incomplete oxidation. Sol gel methods are notorious for the reducing conditions that are present during pyrolysis. In this case, the diffusion is driven by the oxidation of Pb at the PZT/oxygen interface. The Cabrera and Mott model proposes that the ad-

sorption of O_2 on the surface causes electrons to tunnel to the surface creating an electric field that causes drift of the Pb^{2+} ions to form nanocrystalline PbO . The thickness increases parabolically with time and so the process eventually slows. At higher temperatures the drift of electrons to the surface is thermally activated, as described by Wagner [15]. A second, closely related mechanism that could explain this type of segregation is kinetic demixing. Multicomponent oxide thin films are exposed to high thermodynamic potential gradients when they are heat-treated, particularly a gradient of temperature and chemical potential of one or more elements [16]. Thus, the driving forces for the diffusion of mobile species will also be significant. Heat treatments, notably in oxygen, are used to increase the ferroelectric character of the film, a process that creates a steep chemical potential gradient of the oxygen in the film.

The applied gradients create a thermodynamic force that induces fluxes of the mobile components, which can lead to three basic degradation phenomena of the materials.

- The material becomes chemically inhomogeneous (kinetic demixing).
- The material might decompose into new phases (kinetic decomposition).

These phenomena are kinetic in origin, thus, if the thermodynamic potential gradient is removed the fluxes will stop, and the material will tend to become homogeneous again.

Kinetic demixing is often treated for solid solutions, but it has been shown [16] that a single phase can decompose under a chemical potential gradient. Fig. 5 illustrates the case for PZT. If an oxygen concentration gradient exists then the Pb^{2+} , Zr^{4+} and Ti^{4+} species will diffuse at different rates, in the direction of higher oxygen potential. The fastest diffusing species is Pb^{2+} and so it segregates to the surface.

4.3 Ferroelectric properties

The diffusion of Pb or Bi to the film surface is compensated by a flow of Pb/Bi vacancies in the opposite direction, which will create Schottky defects or vacancy pairs with the oxygen vacancies, present in the film, in high concentration after crystallisation. Vacancy pairs pin domain walls and so will affect the imprint characteristics of the film [17,18].

Atkinson discusses the effect of the migration in an ionic solid [19]. The electric field generated in the film is due to the ambipolar diffusion. Generally, metal ions are more mobile than oxygen ions; tracer experiments show that oxygen diffuses into films quickly only along grain boundaries. Electrons must diffuse outwards or holes inwards to ionise the O atoms adsorbed at the surface. Usually electrons are more mobile than metal ions and the surface will develop a

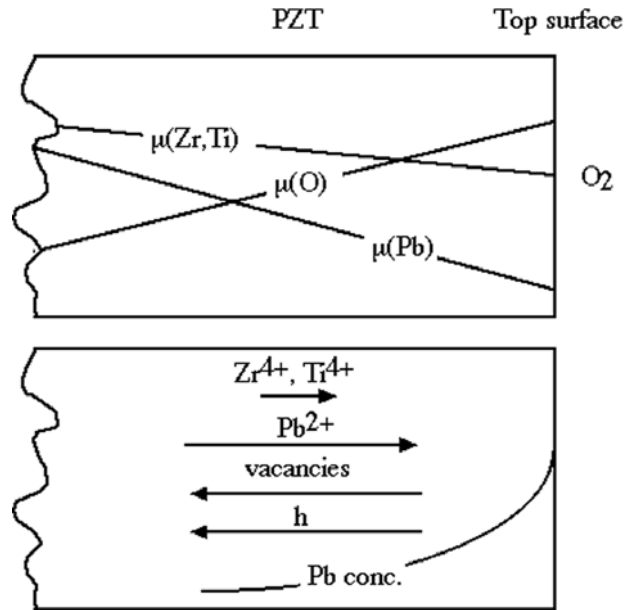


Figure 5. Chemical potential gradients present in a ferroelectric film exposed to oxygen (top); diffusion fluxes of various species (ions, vacancies, holes) and the resultant lead concentration profile (bottom)

negative electric potential relative to the bulk. The same would be true, however, if the film grew by diffusion of oxygen ions. The direction of the electric field vector depends on whether the ions are more mobile than electronic species. Such field near the Curie point could polarise the ferroelectric quite easily. Sometimes the induced polarisation seems to be established by a field that appears to have been positive at the surface [11]; one must consider that ferroelectrics are highly polarisable and ions could be more mobile than electronic species near the ferro/paraelectric transition.

V. Conclusions

Chemical segregation of lead and bismuth to the surface of ferroelectric films has been shown to be real effect and not an artefact of analytical techniques.

The observed surface enrichment seems to confute the proposed hypotheses stating that evaporation leads to surface depletion. In fact, the observed depletion is subsurface and the result of the diffusion that takes place towards the free surface.

This form of phase separation is termed kinetic decomposition, a phenomenon that takes place in thermodynamic potential gradients. Ferroelectric thin films, prepared by sol gel techniques, are subject to steep chemical potential gradients of oxygen, causing the faster diffusing species to separate. Importantly, final annealing in O_2 may be insufficient to oxidise the film as the oxygen vacancies are only compensated by metal vacancies, hence, film fabrication must consider the effects of precursor and sol preparation and con-

trol of the pyrolysis step to ensure adequate oxidation of the ferroelectric oxide.

Kinetic demixing is accompanied by phenomena that significantly influence the electric properties of the films:

- The generation of vacancy pairs $\text{Pb}^{2+}/\text{Bi}^{3+}$ and O^{2-} that are believed to pin domain walls.
- The generation of an electric field in the ferroelectric near the Curie point that can polarise the film during its crystallisation.

It is proposed that the application of models that describe the behaviour of ferroelectric thin films in thermodynamic potential gradients is important for a true understanding of ferroelectric thin films. A deeper understanding of the high temperature transport processes in these materials is necessary.

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