Sol-Gel derived Ferroelectric Thin Films for Voltage Tunable Applications

by Arne Lüker, 28th of May, 2009

Abstract of Ph.D-Thesis

Ferroelectric perovskite thin films for voltage tunable applications, namely (Ba,Sr)TiO_3 (Barium Strontium Tinanate or BST) and (Pb,Sr)TiO_3 (Lead Strontium Titanate or PST), were synthesized via the so-called sol-gel route. While BST showed the tendency to severe film cracking, PST can be grown crack free onto platinised Si standard substrates and even directly onto SiO_2, SiN_x or bare Si.

The growth kinetics of BST and PST on platinised SiO_2/Si were studied in detail using X-ray diffractometry (XRD), scanning electron and atomic force microscopy, SEM and AFM respectively. It was shown that BST fully crystallises at 700°C whereas PST begins to crystallise at 500°C on Ti/Pt and 550°C directly on SiO_2. After a thermal treatment of 650°C for 15 min both PST films were fully crystallised with random (100) and (110) orientation and a smooth surface.

Fig. 1 represents the journey we took within this thesis in terms of the figure of merit (FOM = tunability/dielectric loss) and different ferroelectric perovskite thin films.

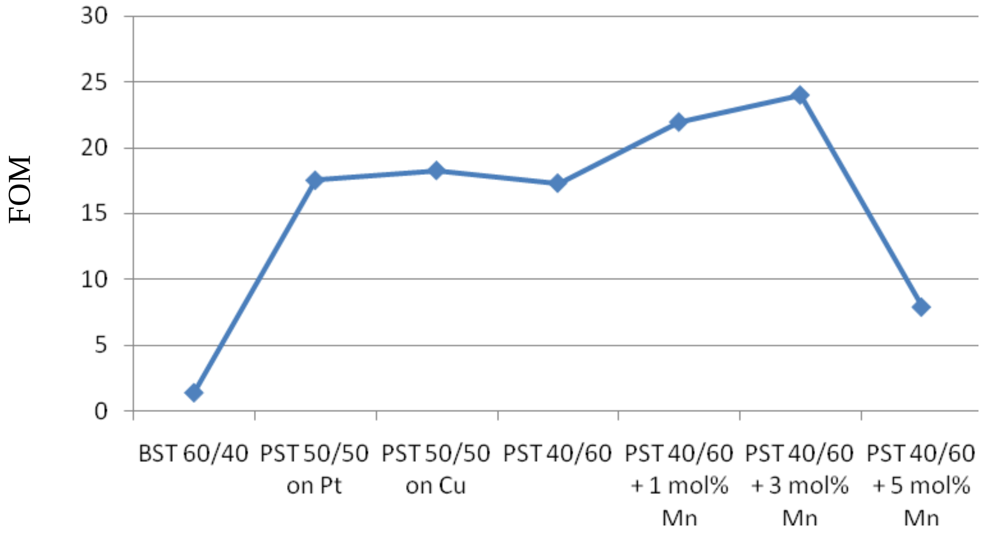

Fig. 1: The figure of merit of different ferroelectric perovskite thin films presented in the thesis.

We started with BST 40/60 thin films with a very low FOM of 1.4 which is a result of severe film cracking during the high temperature annealing bake. With the change to PST 50/50, a system which is very friendly in terms of film cracking, the FOM increased rapidly up to a value of 16.6. A small improvement of 1.65 could be made with the change of the electrode from Pt to Cu. This was explained with the lower resistivity of Cu which increased the quality factor of the overall material system. But is was observed that the response of PST 50/50 to an applied electric field showed a hysteresis indicating that the thin film is in the ferroelectric tetragonal state with a permanent electric dipole moment which in turn increases the loss. By decreasing the Pb content down to 40% the Curie temperature was ensured to be below room temperature viz. the film was in the favoured paraelectric state without a permanent dipole moment. However, the FOM decreased slightly. Doping of the B site with Mn altered the charge balance inside the perovskite film.

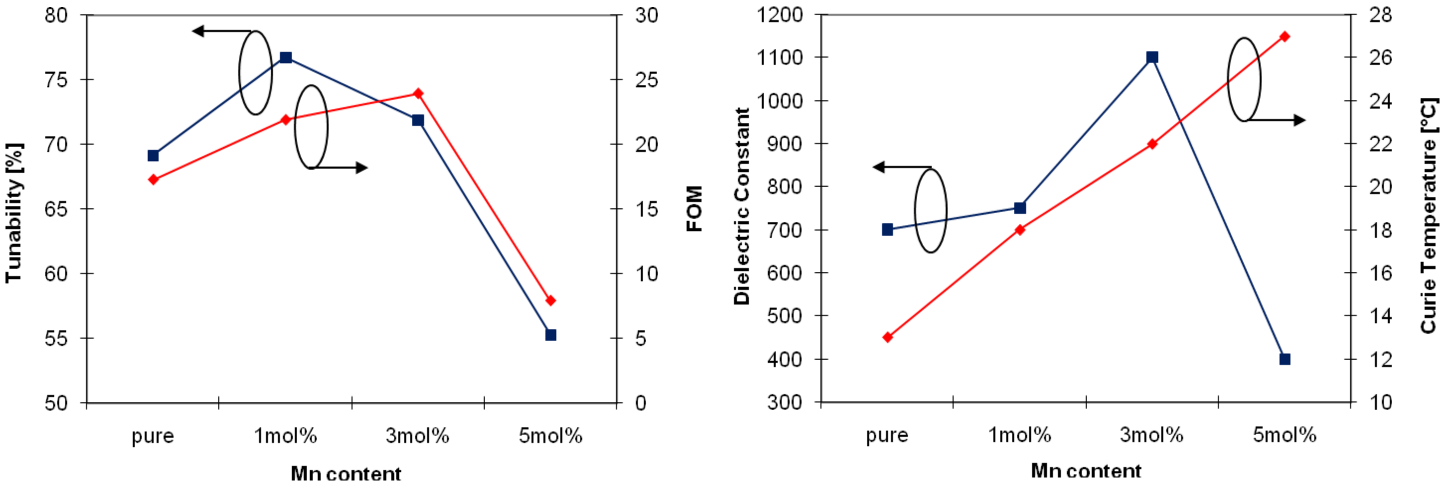

Fig. 2: Tunability and figure of merit at 10V and dielectric constant and Curie temperature at zero bias of PST 40/60 with different Mn content

Fig. 2 summarises the effect of Mn doping in more detail. The dielectric constant reaches a maximum of 1100 with 3 mol% Mn; the maximum value of the tunability with 10 V is 76.72% with 1 mol% Mn and the figure of merit (FOM) reaches 23.96 with 3 mol% Mn. This compares well with results from Du *et al.* [1], who reported a tunability of 80% and a FOM of 14.17 in pure PST 40/60 and 70% and 7 in La doped PST, or Sun *et al.* [2], who achieved a tunability of 69.4% and a FOM of 28.9 in $(Pb_{0.25}Ba_{0.05}Sr_{0.7})TiO_3$.

All these values drop significantly when the Mn doping level exceeds 3 mol% and we identified two different reasons for this behaviour. First, Mn^{2+} doping consumes oxygen vacancies to get incorporated as Mn^{3+} and/or Mn^{4+} at the Ti^{4+} site of the $(Pb,Sr)Ti0_3$

perovskite crystal structure. The negative charged Mn ions balance the positive induced charge of the oxygen vacancies leading to a more “perfect” (cubic) and electronically saturated perovskite. At the same time, more polarisation path may be provided when the lattice structure becomes more perfect. This results in an increase of the dielectric constant, tunability and FOM.

At a doping level of 2 mol% Mn the crystal is totally saturated. With further doping a hopping conduction due to the hopping of the charge carriers between Mn sites begins to occur and becomes distinct in 5 mol% doped films. This type of hopping process is therefore associated with a certain amount of Mn dopant and more Mn amount can provide more pathways for the total hopping process. The dielectric constant, tunability and FOM decrease.

On the other hand the transition temperature from cubic paraelectric to tetragonal ferroelectric increases with increasing Mn content as it can be seen in Fig 2. The Curie temperature is above room temperature with a doping level of 5 mol% resulting in an increased loss mechanism due to the permanent electric dipole moment of the ferroelectric state. This influences the tunability and FOM significant. Hysteresis measurements showed the effect of an enhanced ferroelectric characteristic in Mn doped PST and give raise to the question whether a relaxorlike behaviour is also observable or not.

All these results indicate that PST 40/60 with an Mn content of 2 mol% should result in an optimal ferroelectric thin film for voltage tunable frequency agile applications at room temperature. In combination with Cu electrodes such a device should have superior performance with a very high quality factor.

PST was successfully deposited directly onto SiO_2. This is an important and interesting feature of this perovskite thin film since similar films like PZT or BST blister without an additional seed layer. Pt is the most common metallic layer on which these films crystallise well. It is chemical robust and withstands high temperatures needed for the crystallisation of ferroelectrics. The drawback is the price of this noble material and the relatively high electrical resistivity. The Sr content in PST makes it possible to grow this ferroelectric thin film on SiO_2, SiNx and even bare Si. While Si is a covalently bonded material, PST is an ionic crystal that is unable to form covalent bonds. An electronically saturated Si-PST stack must thus exhibit an interfacial layer which provides a covalent bonding environment towards the silicon substrate and in addition an ionic template compatible with that of PST or $SrTiO_3$. SrO covalently saturates all Si dangling bonds by forming $SrSiO_3$ and/or Sr_2SiO_4. This provides the necessary ionic template towards the perovskite SrO-terminated $SrTiO_3$, on which PST can grow further on. Up to now it is unclear why this is not the case for BST, which cracks and blisters like PZT on SiO_2.

Furthermore the $SrSiO_3$/Sr_2SiO_4 interfacial layer proves to be a fabulous barrier layer which stops not only the Pb diffusion into the Si substrate very efficiently. It inhibits the interdiffusion of all components of PST into the SiO_2/Si and vice versa. This offers the possibility to realise a thin interfacial layer for future integrations of ferroelectrics in all kind of devices like non-destructive read out ferroelectric RAMs [3 - 6] or simply as a buffer layer for the realisation of ferroelectrics onto Si without the common Ti/Pt bottom electrode [3, 7 - 9]. Auger spectroscopy was used to study the compositional change in the interfacial region between PST and PZT thin films and SiO_2/Si substrates to understand the growth kinetics of PST directly onto SiO_2 in more detail. The thin films from both materials are annealed under the same conditions (temperature and time). It is found that strontium stops the lead diffusion into SiO_2 by forming $SrSiO_3$/Sr_2SiO_4 and SrO, maintaining a well defined SiO_2 region, while $PbSiO_3$ is formed in the PZT/SiO_2 system.

A single layer of PST was finally used as a buffer layer for the growth of piezoelectric PZT directly onto SiO_2 to replace the common Ti/Pt bottom electrode. The initial characterisation of PZT device structures showed that PZT films with PST as a diffusion buffer had fully crystallized in the perovskite phase exhibiting good dielectric and ferroelectric behaviour. Although the piezoelectric coefficients of the PZT films were not measured directly in this study, it is envisaged from the experimental data of the dielectric constant and hysteresis loop that the PZT/PST composite has the potential to provide good and comparable piezoelectric performances as typically observed in PZT device structures grown on commonly used Ti/Pt.

A direct comparison between PZT deposited on a common Ti/PT and a PST buffer layer revealed no large differences in the final electrical and piezoelectrical properties of PZT. This is a very promising result for the realisation of piezoelectric functional thin films without the use of a metallic bottom electrode.

All the above presented result are a good framework for further research and investigations. It would be beneficial to increase the viscosity of the actual sol to decrease the number of single layers to achieve thicker films. First trials to thicken it with an higher amount of 1,3-propanediol lead to a thicker single film but poorer performance in terms of tunability and loss. The measurement technique to determine the transition temperature needs to be improved. The homemade kit used in this study was not sensitive enough to measure the frequency dispersion of the maxima in the dielectric constant which is an essential characteristic of relaxor ferroelectrics. Our measurements show that the Curie Temperature increases with increasing Mn content. The peak of the maximum permittivity broadens with increasing Mn content and develops a double peak characteristic with could not be explained at the moment.

A detailed theoretical understanding of the effects due to Mn doping of PST was developed. However, Mn is a special kind of dopant, it is a multivalence ion – it can appear as Mn^{2+}, Mn^{3+} and Mn^{4+}. Especially Mn^{4+} substitutes Ti^{4+} directly and consumes positive charged oxygen vacancies to get incorporated. Therefore it is unclear if one can catalogue this kind of substitution as donor or acceptor doping in the classical sense. It is necessary to use dopants which can be clearly identified, like for instance Nb as a donor or Ni as an acceptor dopant, to develop a full picture of the effect of B side doping of PST.

At the end it is worth pointing out that localised electron hopping between mixed-valence Mn ions provides a possibility to induce double exchange effects of Mn^{2+} and Mn^{3+} or Mn^{4+} and thus brings about magnetic properties [10]. This may be the mechanism behind the magnetic effect in Mn doped $PbTiO_3$ observed by Kumar *et al.* [11]. The coexisting of ferroelectric and ferromagnetic properties in a single PST thin film would provide a fresh method to obtain multiferroics.

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