

Sol-Gel derived Ferroelectric Thin Films for Voltage Tunable Applications

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What are Ferroelectrics?

Piezoelectricity:

Paul and Jacques Curie ~1880
generation of electricity as a result of mechanical pressure and vice versa.

Pyroelectricity:

- · Ancient Greeks in tourmaline
- Sir David Brewster 1824

• spontaneous polarization whose amplitude changes under the influence of a temperature gradient.

Ferroelectricity:

• Joseph Valasek 1920 in Rochelle Salt^(*)

• direction of polarisation can be reoriented by application of an electric field.



^(*) Rochelle Salt, or "sel polychreste" derived from the greek $\pi o\lambda u \chi \rho \eta \sigma \tau o \sigma$, invented by Elie Seignette as a mild purgative in 1665 in La Rochelle, France.

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The Discovery of Ferroelectricity: Joseph Valasek



The first published hysteresis curve



Piezoelectric activity of Rochelle salt vs. temperature indicates the existence of two phase transitions

"Piezoelectric and allied Phenomena in Rochelle salt", meeting of the American Physical Society in Washington in April **1920**: The data ..." is due to a hysteresis in P analogous to magnetic hysteresis. This would suggest a **parrallelism** between the behavior of Rochelle salt as a dielectric and steel as a ferromagnetic substance".

paraelectric

Phys. Rev. **15**, 537 (**1920**): ..."*permanent polarisation is the natural state*" of Rochelle salt. (Master Thesis)



Joseph Valasek 1922

Phys. Rev. **19**, 478-491 (**1922**); "*Piezo-electric activity of Rochelle salt under various conditions*" (Ph.D Thesis).

- Temperature dependence of piezoelectric response
- narrow temperature range of high piezoelectric activity
- indicating the existence of phase transitions (Curie Point)

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^{*)}In an antiferroelectric, unlike a ferroelectric, the total, macroscopic spontaneous polarisation is zero, since the adjacent dipoles cancel each other out 6

$(Ba,Sr)TiO_3$ – the Shift of the Curie Temperature, 1946



• By substituting the the A-site atom (Baatom) with Sr the Curie temperature, T_C , can be shifted down from 130°C to around room temperature .

• The linear drop of T_C is ca. 3.4°C per mol%.



Realisation of the paraelectric state at and below room temperature.

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Temperature of phase transition in solid solution of (Ba, Sr)TiO3 vs. composition (Rushman and Strivens, 1946)

Attractive candidate for voltage tunable devices like varactors, phase shifters, DRAMs etc., where the ferroelectric crystal or thin film should be in the paraelectric state viz. the **operating temperature should be above T**_c

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Landau-Theory

The Theory of the non-linear Response of Ferroelectrics

$$F = \frac{\alpha}{2}P^{2} + \frac{\beta}{4}P^{4} + \frac{\gamma}{6}P^{6} - EP$$

$$\frac{\partial F}{\partial P} = 0 \implies E = \alpha P + \beta P^3 + \gamma P^5$$

$$E = \alpha_0 \left(T - T_0 \right) P + \beta P^3 + \gamma P^5$$

For a Zero Bias Field:

With E=V/d, P=Q/A: $V = \frac{\alpha(T)d}{A}Q + \frac{\beta d}{A^3}Q^3$

F: Helmholtz free energy P: macroscopic polarization E: macroscopic electric field α : Temp. dep. material constant β , γ : Material constant $T_0 \sim T_C$



Lew Dawidowitsch Landau

A: Area D: Distance Q: Charge V: Applied Voltage

$$C_{\max} = \frac{dQ}{dV}\Big|_{V=Q=0} = \frac{A}{\alpha(T)d} = \frac{\varepsilon O(T)A}{d}$$

With $\varepsilon O(T)=1/\alpha(T)$ the temperature dependent dielectric permittivity at zero bias

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Tunability

The Theory of the non-linear Response of Ferroelectrics - non-zero bias field

$$n = \frac{C_{\text{max}}}{C_{\text{min}}} \text{ or } n(\%) = \frac{C_{\text{max}} - C_{\text{min}}}{C_{\text{max}}} \cdot 100$$

It can be shown that the voltage dependent Capacitance can be expressed as:



Where V_2 is the applied Voltage where $C(V)=C_{max}/2$.



Theoretical curve of the dielectric response (blue) compared to measured values of PST 50/50

*) N. Setter et al.; Polar Ceramics in RF-MEMS and Microwave Reconfigurable Electronics: A Brief Review on Recent Issues; Journal of Electroceramics, 13, 215-222, 2004

Loss

tan δ ξ

ξ² ε³

Γο

Skin depth: At 10 GHz:

Al: 814 nm

Cu: 660 nm

Au: 789 nm

Ag: 640 nm

Electrodes

There are different kind of loss mechanisms:

A) Extrinsic loss

General in Films:

Defects and particles in the film •

Due to Measurement (and High Frequencies)

- Electrode loss due to the skin depth
- Fringing fields and parasitic capacitances
- Substrate loss •

B) Intrinsic Loss (Solid State Physics)

- Three-Quantum Mechanism (1): the energy quantum of the electromagnetic field $\hbar\omega$, is absorbed during the collision with two thermal phonons
- Four-Quantum Mechanism (2): ħω is absorbed during the collision with three phonons
- Quasi-Debye Loss Mechanism (3): relaxation of the phonon distribution function (only in the ferroelectric state)*)



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 Ω_0 ω

Low frequency:

 Γ_0 : Damping ~ 100 GHz

 Ω_0 : Soft-mode frequency



Part II

(Ba, Sr)TiO₃

- Sol-Gel Synthesis
- Characterisation and Problems

(Pb, Sr)TiO₃

• PST 50/50, Preparation, Characterisation and Application

- Mn doped PST 60/40, Characterisation
- Oxygen Vacancies and Electron Hopping
- Enhanced Tunability and Ferroelectricity

(Pb, Sr)TiO₃ on SiO₂

- Atomistic Model
- Auger Analysis



(Ba,Sr)TiO₃ – Sol-Gel Preparation



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X-ray Analysis – The Crystallisation of BST

X-ray diffractograms of BST (a) pyrolised at 550°C; annealed at (b) 600°C, (c) 700°C, (d) 800°C, and (e) 900°C for 30 minutes.

Dielectric Properties of BST 60/40

High losses above 200 kHz (30-40%) Tunability ~14% @ 50 kV/cm

Film	Diel. Const.	tanδ	Tunability	K –factor*)
Pure BST50	2714	0.0215	51.87	24.08
BST50:MgO	1277	0.0052	28.48	55.12

Room temperature dielectric properties of the pure and heterostructured BST:MgO films measured at 1MHz and applied electric field of 25.3 kV/cm . Jain et al.

Cracks – a major problem

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(Pb, Sr)TiO₃ – a "good-natured" perovskite

Lattice parameters for (Pb,Sr)TiO₃ vs. Sr content

Phase Transition from tetragonal, ferroelectric, to cubic, paraelectric, at room temperature with a Pb/Sr ratio of ~**50/50**

Only one Phase Transition is known (compared to three in $BaTiO_3$ and $(Ba,Sr)TiO_3$

Easy to realise a crack-free thin film via Sol-Gel

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(Pb, Sr)TiO₃ – Sol-Gel Preparation

XRD Analysis – The Crystallisation of PST

X-ray diffractograms of PST after 15 minutes at (a) 350°C, (b) 400°C, (c) 450°C, (d) 500°C, (e) 550°C, (f) 600°C and (g) 650°C.

Dielectric Properties of PST 50/50

Enhanced Quality Factor with Cu Electrodes

Schematic illustration of the fabrication of Cu/PST/Cu varactors by layer transfer

TEM Analysis of Cu/PST/Cu Varactors

Bright-field TEM of the Cu/PST/Cu varactor

TEM image of the Cu bottom electrode/PST interface

TEM image of the PST/Cu top electrode interface

- Single PST layer thickness ~ 50 nm
- Dark, rough, interlayer between PST and Cu bottom electrode (TiW layer which diffuses into the ferroelectric thin film)
- Sharp interface between Cu top electrode and 1st PST layer (good removal of the Pt/Ti seed layer)
- Sharp interface between 1st and 2nd PST layer (different layer morphology is due to dissimilarities between the films onto which these layers were spun)

B-Site Doping of PST 40/60 (Mn-doping)

Change of composition: Shift of T_C to lower temperatures.

Mn doping has an effect of the grain size of PST:

- PST pure: ~ 100 nm
- 1 mol% Mn: ~ 80 nm
- 3 mol% Mn: indistinct
- 5 mol% Mn: sponge-like

SEM images of $(Pb_{0.4}, Sr_{0.6})(Ti_{!-x}, Mn_x)O_3$. (a) x=0, (b) x=0.01, (c) x=0.03 and (d) x=0.05

Dielectric Properties and Roughness of Mn doped PST

Dielectric Constant and loss vs. frequency forPST 40/60 with different Mn content

- The dielectric constant increases with increasing Mn content up to 3 mol% and decreases there after.
- The roughness/grain size is decreasing with increasing Mn content.

<u>There is no clear evidence that the film</u> <u>roughness/grain size is related to the</u> <u>dielectric behaviour in B site doped PST.</u>

RMS = 3.37 nm

RMS = 2.97 nm

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RMS = 2.09 nm

RMS = 1.69 nm

AFM images of $(Pb_{0.4}, Sr_{0.6})(Ti_{1-x}, Mn_x)O_3$. (a) x=0, (b) x=0.01, (c) x=0.03 and (d) x=0.05. Scan size: $2*2 \ \mu m$

The Reason for the Increase of the Dielectric Constant for x < 0.02

1. Oxygen vacancies are generated by heat treatment

$$2Ti^{4+} \rightarrow 2Ti^{3+} + V_o^{\bullet\bullet}$$

2. Mn is a multivalence ion – it can appear as Mn²⁺, Mn³⁺ and Mn⁴⁺

$$\frac{1}{2}O_{2} + Mn^{2+} + V_{o}^{\bullet\bullet} \rightarrow Mn^{4+} + O_{o}^{X} \qquad \frac{1}{4}O_{2} + Mn^{2+} + \frac{1}{2}V_{o}^{\bullet\bullet} \rightarrow Mn^{3+} + \frac{1}{2}O_{o}^{X}$$

$$= \begin{bmatrix} 2Ti^{4+} + Mn^{2+} + \frac{1}{2}O_{2} \leftrightarrow 2Ti^{3+} + Mn^{4+} + O_{o}^{X} \\ 2Ti^{4+} + Mn^{2+} + \frac{1}{4}O_{2} \leftrightarrow 2Ti^{3+} + Mn^{3+} + \frac{1}{2}O_{o}^{X} \end{bmatrix}$$

Mn²⁺ doping consumes oxygen vacancies in PST to get incorporated as Mn³⁺/Mn⁴⁺ at the Ti⁴⁺ site

Mn doping induces a negative charge and thus balances the positive of the oxygen vacancies. Then with the charge being compensated, the lattice distortion ratio in the system decreases, viz. the lattice structure of $Pb_{0.4}Sr_{0.6}Mn_xTi_{1-x}0_3$ becomes more perfect (cubic). According to the thermodynamic theory, the phase formation ability of the crystal is therefore increased with increasing Mn content up to 0.02. At the same time, more polarisation path may be provided when the lattice structure becomes more perfect. So the dielectric constant of the film is correspondingly increased.

The Behaviour of Dielectric Properties in Mn doped PST

x < 0.02: Mn²⁺ doping consumes oxygen vacancies, thus providing a larger polarisation path. The dielectric constant increases

x ~ 0.02: The positive charge of the oxygen vacancies is totally balanced by the negative of Mn^{2+} , Mn^{3+} , or Mn^{4+} . **The system is saturated.**

x > 0.02: Electron hopping between Mn^{2+} , Mn^{3+} and Mn^{4+} begins. The hopping conduction due to the hopping of the charge carriers between Mn sites begins to occur in 2 mol% Mn doped PST, and then becomes distinct in 5 mol% doped films. This lowers in the end the dielectric constant and increases the loss in PST thin films

The Tunability in Mn doped PST

Tuanability and loss vs electric field at 150 kHz of $(Pb_{0.4}, Sr_{0.6})(Ti_{1-x}, Mn_x)O_3$. (a) x=0, (b) x=0.01, (c) x=0.03 and (d) x=0.05

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Comparison between Measured and Theoretical Tunability

Comparison o fthe measured and calculated tunability of $(Pb_{0.4}, Sr_{0.6})(Ti_{1.5}, Mn_{s})O_{3}$

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The Change of T_C with Mn doping

T_c increases with increasing Mn content

Mn [mol%]	T _C [°C]
0	13
1	17
3	22
5	26

Normalised Permittivities vs temperature of $Pb_{0.4}Sr_{0.6}Mn_xTi_{1-x}O_3$

The origin of the broadening of the peak for 3 mol% and the double peak for 5 mol% Mn is unclear. This could be an indication of **an increasing relaxor behavior of PST** with increasing Mn content. Unfortunately the home-made measuring equipment was not sensitive enough to measure the frequency dispersion of the dielectric maximum, which would be a clear indication for relaxor ferroelectrics.

Enhanced Ferroelectricity with Mn doping

The behaviour of the Hysteresis proofs the enhancement of the ferroelectricity in PST with increasing Mn doping.

The slim loop is a further indication of relaxor-like behaviour *):

Hysteresis loops of $Pb_{0.4}Sr_{0.6}Mn_xTi_{1-x}O_3$.

The film is paraelectric with x=0 and the ferroelectricity improves with x.

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Summary

Tunability and figure of merit at 10V and dielectric constant and Curie temperature at zero biasof PST 40/60 with different Mn content

Improved Performance due to Mn B-site Doping

• Mn²⁺ doping consumes oxygen vacancies (a common defect in ferroelectric thin films)

- For Mn > 2-3 mol% hopping of charge carriers between Mn sites occurs
 - · This degrades the film and its properties

Enhanced Tunability with Mn Doping

Max Tunability ~80% with 2% loss → K-Factor 40

Phase Transition shifts to higher Temperatures due to an enhancement of Ferroelectricity Indication of relaxor-like behaviour in Mn-doped PST

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$Pb_{0.4}Sr_{0.6}Mn_{0.03}Ti_{0.97}O_{3} \text{ directly on } SiO_{2}$

*PST on SiO*₂ and patterned *Pt bottom electrode*

A slotted PST varactor to minimise the variation of the capacitor ares due to mask alignment errors.

• Ferroelectric thin films like PZT and BST often need a metallic-like layer on top of the substrate to promote a crack-free (highly orientated) growth.

• The most common metallic layer is Pt due to its high chemical resistance, relative good lattice match to the ferroelectric film, and its stability to the high temperatures required for the growth of ferroelectric thin films.

• Sometimes it is beneficial from the technological site of view to have the ability to work with a patterned bottom electrode rather than a continuous one.

• PST can crystallise crack-free directly on SiO₂.

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The growth of PST on SiO₂

X-ray diffractograms of one layer of PST deposited directly onto SiO_2/Si and annealed for 15 minutes at (a) 350°C, (b) 400°C, (c) 450°C, (d) 500°C, (e) 550°C, (f) 600°C and (g) 650°C.

Beginning of crystallisation at 550°C. ~50°C more than on Pt/Ti

The growth of PST on SiO₂ – part II

Z: 11.6am (a) RMS: 0.686 Z: 31.6am X: 5.0422 (b) Det WD RMS: 0.777 nm X: 3.0 Mar (c) RMS: 7.095

- The roughness is increasing with annealing temperature from 0.686 to 7.905 nm for 550 and 650 °C respectively, indicating an increase in the crystallinity.
- The little pools have a depth of approximately 2 nm and their number is increasing with annealing temperature while their size is clearly decreasing.

The PST thin film can be regarded to be **fully crystallised** after an annealing bake of 650°C.

Atomistic Model of the Si (100) surface

• On the **unreconstructed silicon** surface the atoms form a square array.

• Owing to a lack of upper bonding partners, each atom has two singly occupied dangling bonds pointing out of the surface.

 Pairs of silicon atoms dimerise, using up one dangling bond per atom to form a dimer bond. This is called the "dimer row" reconstruction (a).

• A second rearrangement leads to the "**buckled row**" reconstruction (b), in which one atom of each dimer lifts up and the other shifts down, resulting in a buckled dimer.

• This buckling causes both electrons to localise in the upper silicon atom of a dimer, whereas the other silicon atom with the empty dangling bond prefers a more planar arrangement.

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The unreconstructed Si (100) surface

The top surface of silicon; (a), the "dimer row" reconstruction, and (b), the "buckled row" reconstruction

The interface between Si and SrTiO₃

• Even at room temperature, the buckling pattern is dynamic, with the dimers executing a kind of **"rocking" motion** or oscillation around the idealized structure. As a result the surface dimers are **chemically very reactive** and can serve as receptors for many types of atoms or even molecules.

The Si-SiO₂ interface. Black atoms are Oxygen

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The two relevant interface structures between silicon and $SrTiO_3$

• Among them <u>oxygen</u> and <u>strontium</u>.

• At one half monolayer, the Sr ad-atoms occupy all favorable positions in the center of four dimers and all dangling bonds are saturated.

• The electronically saturated Si-Sr stack acts as an interfacial layer which provides a **covalent bonding** environment towards the silicon substrate and an ionic template compatible with that of SrTiO₃.

•The perovskite SrTiO₃, being an ionic crystal, can grow on this template and forms a second interfacial layer to PST

Auger Spectroscopy of PST- part I 1 - 21 (PST layer)

Auger spectra of one layer PST and its interface to the Si/SiO2 substrate

Etching time 100 sec per step, ion current 2kV at 0.75µA

Auger Spectroscopy of PST - part II 21 – 40 (SiO₂ layer) and 41 – 60 (getting to the Si-substrate)

Auger spectra of the SiO2 layer (a) and the interface to the Si main substrate (b).

More than 40 etch steps were necessary to reach the Si substrate

Depth profile of 1 Layer PST on SiO₂

Depth profile of one layer PST on SiO_2/Si . The interface regions are clearly visible.

No Pb diffusion into the SiO₂. Sr-Ti diffusion is deeper

The broad SiO₂ area is the dominant feature in this graph and the SiO₂-Si interface is clearly distinguishable

Comparison: Depth profile of 1 Layer PZT on SiO₂

Depth profile of one layer PZT on SiO_2/Si . The interface regions are blurred.

Etching time 100 sec per step, ion current 2 kV at 0.9 µA A triplication in etch cycles was needed to reach a comparable depth Indication of **formation of some lead silicate** (PbSiO₃)

Lead Silicate or not?

Details oft the Auger analysis for Pb, Oxygen and Si in the interfacial region of PZT on SiO2/Si. Black, thick trace: etch cycle 54.

The first two traces after etch **cycles 15 and 32** (top blue and magenta in the Pb and oxygen spectra) show that Pb and oxygen are present in the expected contribution.

After etch cycle 54 a double peak begins to appear in the oxygen and Si spectra.

The **Pb double peak** moves slightly to lower energies and begins to "wobble" around this position with increasing depth until it **vanishes after the 94**th **etch cycle** (second dark blue trace).

After the Pb is not traceable anymore the oxygen shows only one peak at higher energy and the Si only one at lower energy. The oxygen peak is decreasing and the Si is increasing while shifting again to a higher energies with further etch cycles.

The strong relationship between the behaviour of the Pb, oxygen and Si auger electrons confirms the assumption of **the formation of lead silicate in diffusion region**.

Summary

• PST growths directly on top of SiO₂ and/or Si (100)

It growths also on SiNx (not shown here)

The activation temperature is ~50°C higher than on Pt/Ti

Auger Analysis of PST on top of SiO₂

Strontium diffuses slightly more into SiO₂ than Lead or Titanium Clearly defined interfacial regions are visible

Auger Analysis of PZT on top of SiO₂

All Elements of PZT diffuse into the SiO₂ layer

Interfacial regions are blurred

Strong evidence of the formation of Lead Silicate

Part III Conclusions of this Talk

• A theoretical understanding of Ferroelectricity was given; including: Phase Transitions in perovskite Crystals, Curie Temperature, loss mechanisms and the non-linear response of ferroelectrics (in the paraelectric state).

- The Sol-Gel Synthesis of (Ba, Sr)TiO₃ and (Pb, Sr)TiO₃ was presented.
- Problems, e.g. cracking, of BST were identified and remain unsolved.
- PST was presented as an excellent candidate for frequency agile applications.

PST Studies

- Mn B-Site Doping improves the performance significantly.
- Higher Dielectric Constant, lower Loss and enhanced Tunability with an adequate doping level.
- PST onto SiO₂, Si or SiNx without a metallic-like seeding layer is possible and well understood.

Thanks!

