Preparation and characterization of barium-based perovskite dielectrics on different bottom electrodes by chemical solution deposition

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Abstract

Recently, there has been an interest in CSD techniques for the development of barium titanate (BT) based electrolytic capacitors, multi layer ceramic capacitors (MLCC), and embedded passives in printed wiring boards (PWB’s). In order to miniaturize these components further, the dielectric as well as the electrode thickness has to be reduced. Under such circumstances chemical solution deposition methods are increasingly being favoured for deposition of the dielectrics in the near future over other methods due to its simplicity and low precursor costs. While, the commercially available precursors for CSD are cheap, they have certain problems associated with them in terms of residual carbon content (specially under reducing atmospheres with base metal electrodes) and high processing temperatures. Another drawback of CSD based technique is the number of coatings required to achieve mesoscopic thicknesses (500 nm - 800 nm). It is the aim of this thesis to examine new methods of processing at lower temperatures with different bottom electrodes and achieve mesoscopic thicknesses in a few coating steps while maintaining acceptable device properties.

The following processing changes were done in order to lower the crystallization temperature of barium-based perovskites. First, a more reactive atmosphere consisting of a mixture of ozone and oxygen was used to crystallize the films. At temperatures around 650ºC the amorphous films derived from the carboxylate route were found to crystallize. Though such a process did not lower the crystallization temperature, post-annealing treatments in ozone reduce the leakage of the thin films by three orders of magnitude. In the second method, amorphous thin films of approximately 100 nm thickness were deposited on platinized silicon wafers and were subjected to different KrF laser fluences between 100 and 150 mJ/cm². Though the crystallinity increased with increased laser fluences, irradiation above 150 mJ/cm² led to ablation. Even on irradiating with lower fluences the dielectric films developed cracks during crystallization. Cracking was avoided by keeping the substrate at an
elevated temperature of 250°C. This method can be used to crystallize thin films on different substrates where the substrate itself cannot be subjected to high temperature processing. Third, new precursor solutions based on aminoethoxides of barium and strontium were synthesized. By use of these carboxylate free precursors the formation of the intermediate oxo-carbonate phase was avoided. This method led to lower the crystallization temperature to 600°C.

Both A-site and B-site substituted BT based thin films were fabricated on Ni electrodes. BT, BST and BTZ thin films of thickness around 600 nm were deposited by 12 multiple coatings. The pyrolysis and the crystallization procedures were optimized into 4 consecutive depositions followed by a crystallization step. This procedure was repeated thrice to achieve a thickness of 600 nm in 12 coating steps. Tunability and frequency dispersion for the different compositions was analysed with respect to processing temperature and post annealing treatments. The possibility to use CSD for the deposition of thin film dielectrics for future MLCC’s with thinner dielectric layers was shown.

Finally a new method of deposition of hybrid solutions based on a mixture of microemulsions and CSD solutions (µECSD) was developed. The novelty of this method lies in the fact that films of mesoscopic thickness (500 nm – 800nm) can be deposited with only a few deposition steps. With these hybrid solutions such thicknesses can be achieved with only 5-8 steps depending on the amount of the MOD solution present in the hybrid solution.
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Symbols and Abbreviations

\[ \alpha \] Absorption coefficient
\[ \varepsilon_0 \] Permittivity of free space
\[ \varepsilon \] Permittivity
\[ \nu \] Frequency
\[ \lambda \] Wavelength
\[ n \] Refractive index of film
\[ n_0 \] Refractive index of air
\[ n_s \] Refractive index of substrate
\[ k \] Extinction coefficient

ALD        Atomic Layer Deposition
BHT        Barium Hafnate Titanate, \( \text{Ba(Hf}_x\text{,Ti}_{1-x}\text{)}\text{O}_3 \)
BST        Barium Strontium Titanate, \( \text{(Ba}_x\text{,Sr}_{1-x}\text{)}\text{TiO}_3 \)
BT         Barium Titanate \( \text{BaTiO}_3 \)
BTZ        Barium Titanate Zirconate, \( \text{Ba(Ti}_x\text{,Zr}_{1-x}\text{)}\text{O}_3 \)
CSD        Chemical Solution Deposition
CVD        Chemical Vapor Deposition
DTA        Differential thermal Analysis
EXAFS      Extended X-ray Absorption Fine Structure
GIXRD      Glancing Incidence X-ray diffraction
LTCC       Low Temperature Co-fired Ceramics.
µE-CSD     Microemulsion Chemical Solution Deposition
MEMS       Microelectromechanical Systems
MIM        Metal-Insulator-Metal
MLCC       Multi Layer Ceramic Capacitor
MOCVD      Metal organic Chemical Vapor Deposition
MOD        Metallo-organic Deposition
Ni         Nickel
PLD        Pulsed Laser Deposition
PWB        Printed Wiring Board
PZT        Lead Zirconate Titanate, \( \text{Pb(Zr}_x\text{,Ti}_{1-x}\text{)}\text{O}_3 \)
RTA        Rapid Thermal Annealing
SEM        Scanning Electron Microscope
ST         Strontium Titanate, \( \text{SrTiO}_3 \)
TGA        Thermogravimetric Analysis
UV-VIS     Ultraviolet Visible
XRD        X-Ray Diffraction
YBCO       Yttrium Barium Copper Oxide, \( \text{(YBa}_2\text{Cu}_3\text{O}_{7-\delta} \)
Chapter 1

Introduction

Chemical solution deposition\(^1\) (CSD) methods for electronic oxides have been used for almost 2 decades in a variety of applications. Compared to other deposition processes these methods offer some advantages such as homogeneity, excellent control over stoichiometry and ability to coat large area substrates. The most widespread use of these methods is in antireflective coatings with refractive index gradation\(^2\), optical or infra red absorbing coatings\(^3\), electrically conductive oxides\(^4\) and coatings that protect against scratch, oxidation and erosion on different types of materials. Recently, sol-gel or rather CSD based processes for 4- or 32 Mbit FeRAM prototypes have been demonstrated by the industry\(^5\), although methods like MOCVD\(^6\), sputtering or atomic layer deposition (ALD)\(^7,8\) have advantages due to the potential for conformal coverage of small 3-D structures. CSD methods are a cheaper way to study the behavior of different electronic oxide thin films quickly and effectively without the need for large investments.

Recently, there has been an interest in CSD techniques for the development of barium titanate (BT) based electrolytic capacitors\(^9\), multi layer ceramic capacitors (MLCC), and embedded passives in printed wiring boards (PWB’s). For all of these technologies, in order
to miniaturize further, it is not attractive to use any of the previously mentioned vapor deposition methods except chemical solution deposition methods mainly due to cost reasons. Manufacture of coated conductors is another area where CSD based methods is used extensively at present\textsuperscript{10}. Usually the chemical solution deposition methods used are spin-coating, dip-coating or various types of spray coating of the precursor solution.

### 1.1 Background of the problem

The properties of the barium-based perovskites, which are the usual constituents for most MLCC’s (fig. 1.1), depend on a variety of factors like processing, electrodes and substrates. Present microelectronics industry uses a variety of substrates for different applications. Substrates can affect the dielectric and electrical properties of thin films in a number of ways. Lattice parameter mismatch between substrate and the dielectric film can enhance or diminish dielectric properties depending on the chosen material system. Also, any change in electrodes will warrant changes in processing parameters. For example, usually for thin film studies platinized silicon wafers are used, but, for MLCC’s and PWB’s base metal electrodes are used. When base metal electrodes are used it is mandatory to use reducing atmospheres while crystallization. This in turn would require the use of various types of dopants and recovery anneals to optimize electrical properties. One of the main problems with the integration of barium based perovskites with semiconductors is its high processing temperatures. For reliable electrical properties, perovskite based dielectrics typically require temperature anneals of 700°C and more. Such high temperatures may destroy underlying device architectures. Hence, the use of these high-$k$ materials has been limited with semiconductors.

Barium based perovskites have been used for a long time in the MLCC industry\textsuperscript{11,12}. This was mainly because the fabrication of MLCC’S and other capacitors were done separately and then surface mounted as passive devices on the board. So temperature and
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atmospheres were never a constraint. With the drive towards miniaturization now the need is to have embedded devices and MLCC’s, which will be much smaller and faster than, used previously. As devices get smaller and smaller the use of high-\(k\) materials is inevitable and there are few non-lead based dielectrics, which can compare with the robustness of these materials. Thinner dielectric and metal electrodes would be required to achieve larger capacitance densities but commercial methods like tape casting used till date for the fabrication of these MLCC’s cannot realize dielectric layers below 800 nm. This is primarily due to the fact that beyond a certain size it becomes difficult to make sufficiently small particles for the green paste. Furthermore, core shell structured particles, which are required for a flat temperature coefficient of capacitance, are difficult to synthesize in such small dimensions.

![Multilayered Ceramic Capacitor](image)

**Fig.1.1.** A multilayered ceramic capacitor.

Therefore the development of processes to deposit dielectric layers of *mesoscopic* thicknesses (between 500 nm and 800 nm) is increasingly becoming important. Modified CSD methods and microemulsions are being investigated currently to deposit films in this thickness range with a minimum number of coatings.
Future trends of embedding capacitors into the PWB’s (Figure 1.2) require new techniques to deposit and fabricate them. It is manufactured by coating the dielectric layer on copper foil, which is laminated together and then used in the manufacture of PWBs (Figure 1.3).

Screen-printing and other techniques, which can fabricate down to thicknesses of around 1 µm are fast becoming obsolete for all the above cases. Availability of smaller discrete components will soon become a limitation during the process of integration.
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Chemical solution deposition methods can be used to bridge this gap of fabrication of dielectrics of mesoscopic thickness (500nm - 800 nm) with slight modifications, which would reduce the number of coatings to achieve a desired thickness. This would necessitate the development of new precursors and also new processing parameters suitable for fabrication.

The electrodes in all the above applications are usually base metal electrodes and therefore processing of the thin films is different. Actually there are two different issues here, the first is the dielectric and the second is the electrode. To process thin films in conjunction with base metal electrodes a reducing atmosphere is mandatory. When using chemical solution deposition methods usually carboxylate based precursors are used which are commercially available and cheap. As long as the perovskites based thin films are fabricated at high temperature and in an oxygen atmosphere excellent results can be obtained. But, if there is a need to fabricate thin perovskite films for devices at temperatures below 650°C it is almost impossible to get reliable electrical properties. The reason usually given for the high temperature crystallization of perovskites is the formation of an intermediate oxocarbonate phase, which decomposes above 650°C. The electrode is another important issue. Final device properties depend greatly on the electrode. Stress on the electrodes can ameliorate or deteriorate dielectric properties. For example results on foils are completely different to that on electroded silicon or other single crystal wafers. As the devices get smaller the electrodes also get thinner and often this high processing temperature leads to instabilities in the electrodes.

Therefore, in view of the aforementioned challenges it would be beneficial for both the MLCC and the semiconductor industry to have thin films of barium based perovskite dielectrics at lower temperatures. Also if these CSD based methods can be used for the deposition of dielectrics of mesoscopic thickness in conjunction with base metals in a few steps it would be highly advantageous for future miniaturization of MLCC’S and embedded capacitors.
1.2 Objectives

(a) To deposit barium titanate and other substituted barium titanate thin films on platinized silicon wafers at lower temperatures and optimize their processing conditions. To use new precursors for chemical solution deposition in order to avoid the formation of the oxo-carbonate phase and check if more reactive atmospheres like ozone have any effect on crystallization. Low temperature processing would be beneficial to both the semiconductor and MLCC industry.

(b) Deposit barium based perovskite materials on nickel bottom electrodes and study their dielectric property based on thickness variations and crystallization temperatures by CSD. The deposition of thin films of BT and substituted BT could be used in the future for further miniaturization of MLCC’s, which still use tape casting methods. Since the doctor blade and screen-printing methods cannot be used effectively to achieve dielectric layers below 1 µm because formation of the ceramic particles at smaller dimensions is difficult. Hence a CSD method would be ideal for future MLCC applications where thicknesses between 500 and 800 nm are foreseen.

(c) Possibility of depositing films in the mesoscopic (500 -800 nm) thickness range by hybrid solutions consisting of nanoparticle dispersions and MOD solution. Only MOD based solutions require a large number of coatings to reach such thicknesses. Such hybrid routes would decrease the number of coatings required to achieve the aforementioned thicknesses.
Chapter 2

Chemical Solution Deposition

The development of chemical solution deposition methods for thin films dates back to mid-80s. Ferroelectric BaTiO$_3$(BT) films prepared by sol-gel methods were first reported by in 1984$^{13}$, followed by PbTiO$_3$(PT), Pb(Zr,Ti)O$_3$ (PZT)$^{14}$. Also superconducting YBCO and thallium-based films have been prepared by sol-gel methods by several groups$^{15,16}$. The early work by these investigators and others led to a rapid expansion of research in this area of electronic oxide thin films. The general principle involved in the chemical solution deposition of perovskite films is to prepare a ‘homogeneous’ solution of the cations, which could be later used for various methods of spray coating or spin coating or dip coating substrates. The fabrication of thin films by this process involves four basic steps:

I) Synthesis of the precursor solution with the desired cations

II) Deposition of the solution by spin-coating or dip coating

III) Low temperature heat treatment for the removal of the organics (drying and pyrolysis) and formation of an amorphous film

IV) High temperature heat treatment for the crystallization and densification of the amorphous layer
Depending on the solution route and the material different thermal processing conditions may be employed to control the film densification and crystallization in order to have materials with optimized properties. Since these films deposited by CSD are often used for electronic applications even slight changes in the processing conditions can alter the microstructure thereby leading to changes in the electronic properties.

Metallo-organic compounds are generally dissolved in a common solvent during the preparation of the precursor solution. The starting reagents are typically metal alkoxide compounds, $\text{M(OR)}_{\text{x}}$, metal carboxylates, $\text{M(OOCR)}_{\text{x}}$ and metal $\beta$-diketonates. The selection of the starting compounds is dictated by a variety of factors like solubility, reactivity, decomposition pathway and stability. The solution route used usually determines the degree of intermixing of the cation species, like formation of a network or individual inorganic phases and the carbon content in the films. Other issues like the temperature at which pyrolysis of the organic species start, the weight loss associated with oxide formation, the densification and crystallization behavior of the films are also greatly influenced by the route. Solution chemistry variations can make a lot of impact on the processing behavior of the as deposited film. Another critical aspect of the precursor solution is the substrate wetting ability. Film properties that can necessitate changes in the solution chemistry include poor thickness uniformity, crack formation, crystallization behavior, microstructure and compositional non-uniformities.

### 2.1 CSD processes

The most frequently used CSD approaches for the production of perovskite thin films maybe grouped into three categories:

1) Sol-Gel processes
2) Metal Organic Decomposition (MOD)
3) Hybrid Processes
Chemical solution deposition and fabrication of films

Other approaches have been used, but less extensively, like the Pechini Process\textsuperscript{17}, citrate route and the nitrate route\textsuperscript{18}. Recently a new type of CSD process has been developed involving microemulsions for the deposition of thicker films for electronic component fabrication\textsuperscript{19}.

The chemical interactions that take place between the starting reagents will depend on both the reactivity of the compound and the solution preparation conditions. In true sol-gel processing routes, the reactivity of the reagents is high, and if alcohol exchange occurs or if modifying ligands are used, the structure of the species in solution can bear little resemblance to the starting compounds. The species that are generated are frequently oligomeric in nature and can contain more than one type of cation. In contrast the carboxylate compounds that are usually used have low reactivity and the chemical interaction between the different precursors is minimal.

2.1.1 Sol-Gel Process

Classical sol-gel processes are the ones which use alkoxides that undergo hydrolysis and polycondensation. Although many different types of alcohols have been used, the solvent 2-methoxyethanol (CH\textsubscript{3}OCH\textsubscript{2}CH\textsubscript{2}OH) has been used most extensively for the preparation of perovskite thin films. Processes based on alkoxides are usually considered to be the most appropriate examples of sol-gel processes since the key reactions of hydrolysis and condensation, in which metal-oxygen-metal (M-O-M) bonds are present.

- **Hydrolysis**

\[
M(OR)_{x} + H_{2}O \rightarrow M(OR)_{x-1}(OH) + ROH \quad (2.1)
\]

- **Condensation (alcohol elimination)**

\[
2 \ M(OR)_{x-1}(OH) \rightarrow M_{2}O(OR)_{2x-3}(OH) + ROH \quad (2.2)
\]

- **Condensation (water elimination)**

\[
2 \ M(OR)_{x-1}(OH) \rightarrow M_{2}O(OR)_{2x-2}(OH) + H_{2}O \quad (2.3)
\]
Pre-hydrolysis of less reactive alkoxides may be used to improve solution compositional uniformity. Often an alcohol exchange reaction results in decrease of hydrolysis sensitivity like the mainly used titanium tetra \textit{i}-propoxide and zirconium tetra \textit{n}-propoxide in the production of PZT. During an alcohol exchange process a less reactive alkoxy group (2-methoxyethoxy group in this case represented by OR') replaces a more reactive alkoxy group (OR).

\[
M(OR)_x + xR'OH \rightarrow M(OR')_x + xROH
\] (2.4)

2-Methoxyethanol has often been used for the dissolution of carboxylate precursors like lead acetate ( Pb(OCOCH\textsubscript{3})\textsubscript{2} ). A typical process involves refluxing of the carboxylate and the alkoxide in separate reaction vessels and then combined together. This is followed by further refluxing, distillation and dilution to the desired concentration. Prior to the deposition of the film the stock solution was partially hydrolyzed to promote oligomerization\textsuperscript{20}. Similar reactions between precursor compounds and 2-methoxyethanol have been also noted in the processing of Pb(Zn\textsubscript{1/3},Nb\textsubscript{2/3})O\textsubscript{3}. Some studies have elucidated that the precursors formed in lead zirconate titanate and lead titanate deposition solutions are apparently small, mixed oligomers\textsuperscript{21,22}. There are also indications that the A-site precursors may not be intimately involved in the formation of the gel network\textsuperscript{23,24}. Sengupta \textit{et.al.} in their EXAF study have shown that different networks of Ti-O-Ti, Zr-O-Ti and Pb-O-Pb within the gel structure exist, thereby clearly indicating that homogeneous mixing of the starting agents had not taken place.

There have been a number of efforts for the synthesis of stoichiometric precursors with structures similar to the crystalline phase of the final perovskite, in order to lower the crystallization temperature. Most of these attempts have resulted in a mixed metal species with a cation stoichiometry different from that of the required perovskite material\textsuperscript{25,26}. Furthermore these complex synthesis procedures have not led to any benefits in terms of processing temperatures or electrical properties.
2.1.2 Metal Organic Decomposition

Metal organic decomposition (MOD) routes utilize carboxylate precursors that do not undergo significant condensation reactions during either solution preparation or film deposition. The basic approach is to simply dissolve the metal-organic compound (e.g. carboxylate or β-diketonates) such as lead 2-ethylhexanoate, zirconium neodecanoate and titanium di-methoxy dineodecanoate in a common solvent like xylene. There is little chance of oligomerization in such a process since the starting compounds are water insensitive. Often the precursor species are similar to the starting compounds. Such processes have been used for the synthesis of a number of ferroelectric materials\textsuperscript{27}, colossal magnetoresistive materials\textsuperscript{28} and superconductors\textsuperscript{29}.

From the first look the MOD process appears simple and easy, but there are quite a few drawbacks. Since the carboxylates used in MOD are usually long chain ligands they often cause cracking during the thin film processing due to excessive weight loss and shrinkage. To avoid this rigorous control of the thermal processing parameters and the solution concentration is required. Another limiting factor is the minimal reactivity of the starting reagents. Here control of structural evolution and film microstructure become limited to variations in solvent, solution concentration, film deposition and heat treatment conditions. Standard MOD process using large carboxylate compounds is still widely employed but it was Haertling who developed an alternative MOD strategy that minimized cracking.\textsuperscript{30} Instead of using the long chain esters/carboxylates he used short chain carboxylate (e.g. acetate) and strongly chelating β-diketonate compounds (e.g. acetylacetone). The use of chelating agents like acetylacetone can lead to the formation of monomeric compounds and lower the organic content of the film. This reduces film shrinkage during drying and decreases cracking. Although the solutions are water insensitive, the presence of carboxylate ligands with alcohols leads to esterification. Solutions, therefore, still exhibit aging and display changes and films produced from such aged solutions differ in property.
2.1.3 Hybrid processes

Hybrid processes are those in which the A-site precursors are carboxylate based precursors and B site precursors are alkoxides. These processes are called ‘hybrid’ because they use both carboxylates and alkoxides. The A-site carboxylate precursor is usually dissolved in the corresponding carboxylic acid because of their limited solubility in alcohols. When mixed the B-site alkoxide precursors react with carboxylic acid to form oligomers. For e.g

\[ n\text{Ti(OR)}_4 + 2n \text{R’COOH} \rightarrow \text{RO[-Ti-O-](OOCR’)}_2\text{R} + \text{ROH} \]  

(2.5)

As shown above these routes rely heavily on the molecular modification of the alkoxide compounds, through reactions with other carboxylic acids (acetic and propionic acids). Usually the carboxylate groups, co-ordinate in a bidentate way with the B-site cation, thereby acting as bridging ligands. This chelation of the B-site cation leads to precursors which are less sensitive towards hydrolysis. 2-4 petanedione (acetyl acetone) is often used as a chelating agent for the B-site alkoxides.

Spectroscopic techniques have been used extensively to study the reactions occurring during the preparation of PZT and BT solutions\textsuperscript{31,32}. PZT and PT gels studied by Sengupta et.al.\textsuperscript{33} by EXAFS indicate separate networks of Ti-O-Ti, Zr-O-Ti and Pb-O-Pb and it is also believed that the A-site precursors are not intimately involved in the formation of gel network for BT for sol-gel processes involving 2-methoxyethanol solvents. In comparison to 2-methoxyethanol processes, hybrid processes are advantageous in some respects. They are easier to synthesize, since distillation and refluxing strategies are sometimes not required, depending on material systems. For synthesis of a typical BT solution usually the barium acetate or propionate is dissolved in the corresponding acid. The titanium alkoxide is stabilized with acetylacetone and then these two solutions are mixed together. While these chelate processes are simple and quick, there are some drawbacks. Continued reactivity in the
solution can change the precursor solution characteristics. The main problem is the increase in water content in these solutions as esterification progresses with time. Water generated during esterification may attack the metal species and finally precipitate them. Boyle et al. have performed a detailed analysis on the timescale of such processes and their impact on the PZT film properties. In spite of these disadvantages, as with sol-gel processes, thin films with excellent electrical and microstructural properties have been prepared by this approach.

### 2.1.4 Micro emulsion CSD (µECSD)

The term microemulsion was first used by Schulmann et al. in 1959 for colloidal systems which are thermodynamically stable, optically isotropic dispersions of two non-miscible liquids stabilized by amphiphilic compounds. These solutions are structured solutions with domains of about 100 nm or less dispersed in a continuous phase. Microemulsions can be formed in oil/water/surfactant mixtures depending on the composition and temperature. At constant concentration of non-ionic surfactant, low oil content and low temperatures, small spherical micelles can be found in emulsions in which the oil is solubilized. This type of microemulsion is called oil-in-water microemulsion (o/w microemulsion). At low water content and high temperatures, small water droplets stabilized by surfactants are present in a continuous oil phase. These systems are called water-in-oil microemulsions (w/o emulsions). For ionic surfactants the phase behavior is reverse. Systematic investigations on many ternary mixtures of surfactant, water and oil or more complex mixtures yield a variety of different structured liquids, which are microemulsions or related systems. The schematic isothermal ternary phase diagram (fig. 2.1.4.1) of a water/surfactant/oil system shows the different structures which can be obtained by varying the composition.
One of the most promising uses of microemulsions is the synthesis of organic and inorganic nanoparticles. Water droplets of diameter less than 100 nm are dispersed in oil by adding surfactants or surfactant/co-surfactant mixtures. Noble metal particles, sulphides, hydroxides, carbonates and oxalates can be obtained by mixing two types of emulsion, one containing the metal ion and the other containing a suitable reagent. Calcination of the hydroxides, carbonates and oxalates yields the corresponding oxides as nanopowders. Alkaline earth titanates and zirconate nanoparticles can also be synthesized by this method.

In this case water in the microemulsion was itself used as a reactant and so a large particle concentration could be achieved. Nanocrystalline BaTiO$_3$ powders with a very narrow particle size distribution can be obtained by a selective hydrolysis reaction of stoichiometric mixture of moisture sensitive metal alkoxides using microemulsion as reaction medium. Once synthesized, these colloidal solutions can be used for a variety of purposes from synthesis of nanoparticles, thick/thin films to nanocrystalline ceramics. However these emulsions when used for the preparation of thick films often suffer from higher porosity due to the large load of organic material which has to be burned off during processing. In order to fill the pores and make these films denser a mixture of these microemulsions with CSD solutions has been used.

![Figure 2.1.4.1 Schematic ternary isothermal section through the phase diagram water-oil-surfactant.](image)
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suggested. These suspensions of BaTiO$_3$ particles can be used with CSD derived solution to
achieve thicknesses in the mesoscopic range (300 – 800 nm), since traditional tape casting
methods cannot deposit films of thicknesses lower than 1 $\mu$m and using pure CSD methods to
deposit films in this mesoscopic thickness range is tedious. Therefore the use of this type of
microemulsion mixed CSD solutions can be an effective alternative in the production of
smaller MLCC’s, MEMS and LTCC modules$^{16}$.

2.2 Coating methods

Precursor solutions synthesized by the above routes have to be coated onto substrates
before it can be of any use. There are various methods of applying these precursor solutions
onto different types of substrates like spin coating, spray coating or dip coating. Each has its
advantages and disadvantages and accordingly different industries use them$^{41}$.

Spin coating (fig. 2.2.1) is usually done with a photoresist spinner which can be
programmed to accelerate rapidly to 4000rpm or more. Substrates are usually silicon or
electroded silicon or single crystals or even foils with slight modifications in the chuck. The
substrate is held at its place by applying a vacuum on the substrate through the chuck. Once

![Processes occurring during spin coating.](image)

Figure 2.2.1 Processes occurring during spin coating.
the substrate is fixed on the chuck the precursor solution is dispensed on the substrate after filtering it through Teflon filters. In the spin-up stage the liquid flows radially outward, driven by centrifugal force. In the spin-off stage, excess fluid flows to the perimeter and leaves as droplets. As the film becomes thin, the rate of removal of excess liquid by spin-off slows down, because the thinner the film, the greater the resistance to flow, and because the concentration of the nonvolatile components increases raising the viscosity. In the fourth stage evaporation takes over as the primary mechanism of thinning. An advantage of the spin-coating method is that a film of liquid tends to become uniform in thickness during spin-off and once uniform tends to remain so, provided that the viscosity is not shear dependent and does not vary over the substrate\textsuperscript{42}.

![Figure 2.2.2 Scheme of the aerosol deposition process.](image)

*Figure 2.2.2* Scheme of the aerosol deposition process.

*Spray coating* can be used where the requirement is conformal film deposition over different non-planar structures (steps, trenches, stacks)\textsuperscript{43}. Usually the precursor solution is converted to an aerosol by a nebulizer (fig.2.2.2). The concentration of the precursor solution
Chemical solution deposition and fabrication of films

is very low in this case because viscous solutions cannot be effectively converted to aerosols. The mist generated by the nebulizer is carried into the deposition chamber by a carrier gas where it settles on the wafer surface by gravitation or by the application of an electrostatic field. In the latter case the aerosol is electrically charged by a corona discharge before entering the chamber. Usually the step coverage is conformal in nature and there are reports of it being successful till 200 nm thickness. The key to conformal coverage is the reduction of the nozzle size of the nebulizer.

![Diagram of dip coating stages](image)

**Figure 2.2.3** Processes occurring during dip coating.

*Dip coating* (fig2.2.3) is another deposition method widely used these days. The batch dip coating can be divided into five stages: immersion (a), startup (b) deposition(c) and drainage (d) and evaporation (e). With volatile solvents, such as alcohol, evaporation normally accompanies the start-up, deposition, and drainage steps. The continuous dip coating
process(f) is simpler because it separates the immersion from the other stages, essentially eliminates start up and hides drainage in the deposited film. This process is used for coating tapes and wires. Dip coating can also be used for sequential coating of complex geometries for capacitor applications. One example is the coating of barium on porous titanium electrodes. The basic principle of fabrication is the same as of tantalum oxide capacitors, the only difference being the electrodes and dielectric material in this case. In tantalum oxide capacitors the dielectric tantalum oxide is deposited electrochemically on the anode tantalum and the cathode is usually a conductive polymer or MnO₂. Since the dielectric constant of Ta₂O₅ is much lower than BaTiO₃, in the near future it would be more attractive to deposit BaTiO₃ based dielectric thin layer on such a capacitor structure. Recently there has been a lot of effort for the fabrication of such BT based electrolytic capacitors (figure 2.2.4). In order to do so first the porous metal anode is fabricated and then this porous electrode is dipped into a solution of BT or barium (depending on the electrode), crystallized and finally the cathode is applied also by dip coating into a solution of Mn(NO₃)₂ (for MnO₂) or polymer cathode.

![Figure 2.2.4 Structure of an electrolytic capacitor.](image-url)
2.3 Drying, pyrolysis and crystallization

Once the film has been deposited on the substrate, to obtain the desired phase, solvent remaining in the body of the film and the organic moieties associated with the gel network have to be removed. During the heat treatment the gel network undergoes a variety of bond reorganizations and structural relaxation processes that eliminate structural free volume within the film. During this process, M-O-C and M-O-H bonds are broken and there is formation of a M-O-M network. This concept of M-O-M network is perhaps somewhat more appropriate for processing the lead based materials, where the formation of an amorphous structure is a distinct material state. In the processing of CaTiO$_3$, BaTiO$_3$, SrTiO$_3$, BaZrO$_3$, the formation of carbonate compounds during pyrolysis further complicates the matter. Two approaches are commonly used for the transformation of the as-deposited film into the crystalline form.

1) Two-step process

In the two-step process, the films are first heat treated, for a short time, between 200 and 400°C during which most of the organic species are removed prior to a longer high temperature crystallization step. During the initial drying and pyrolysis step the films may shrink by 50-70%. Since it is quite common that the thicknesses between 500nm and 2µm are required, often they are fabricated by a multilayer process wherein deposition is immediately followed by pyrolysis (200-400°C) before a final crystallization (600-800°C). Sometimes the deposition and pyrolysis steps are repeated before a final crystallization of the film. This method is usually preferred for PbTiO$_3$, Pb(Zr,Ti)O$_3$ and other lead based systems. The main reason here is that for lead based systems, repeated high temperature crystallizations after each layer deposition would lead to more lead loss and non-stoichiometry. Furthermore the nucleation is always heterogeneous (i.e. at the film and bottom electrode interface) thereby leading to columnar structures with high dielectric constant. So a two step process yields better results.
2) One-step process

In the one-step process the film is directly heated to the crystallization temperature, after deposition, which results in both organic removal and crystallization. Due to the single step nature of the approach a number of complex and potentially overlapping processes may occur during this one single step. One step processes are more preferable for the crystallization of BT, ST and BTZ films. This is because unlike lead based systems, here the nucleation is predominantly homogeneous, and if a two step process(with only one final crystallization) like the one previously mentioned is followed, it would lead to small polycrystalline grains. So, in order to force heterogeneous nucleation a lower solution concentration is used and each layer is directly crystallized in the diffusion oven. Two-step processes can be performed but in such a case pyrolysis and crystallization have to be carried out after each and every deposition step.

2.4 Solution concentration

Another important parameter for microstructure is the solution concentration. For Pb based systems the nucleation is predominantly heterogeneous i.e. at the platinum and film interface but for barium-based perovskites it is always homogeneous. The reason for the homogeneous nucleation of BT based systems is the initial formation of TiO$_2$ nanograins at lower temperatures, which then react with the surrounding BaCO$_3$ matrix to form BT at a higher temperature. This has been proved by Gust.et.al.$^{47}$ by transmission electron microscope (TEM) studies. Recently, the reaction between BaCO$_3$ and TiO$_2$ to form BT has been proved thermodynamically to be the most appropriate in terms of free energy considerations. Hence it would be quite appropriate to infer that the Ba-oxocarbonate or carbonate formed during the decomposition of barium carboxylates reacts with the TiO$_2$ in order to from BT. Therefore, if the amount of the matrix is reduced, a sort of heterogeneous nucleation is forced thereby, favoring a columnar growth similar to Pb based perovskites$^{44}$. The amount of amorphous
Chemical solution deposition and fabrication of films

matrix is reduced by simply reducing the solution concentration (0.1M). Schematically this has been shown in the following figure.

Figure 2.4.1 (a) Homogeneous nucleation and (b) forced heterogeneous nucleation. The circles depict the initial nucleating zones comprising of the nano TiO$_2$ regions surrounded by the barium containing matrix.

When using a solution concentration of 0.1M it leads to films of around 8nm per layer and the for 0.3M solutions it is usually 27nm (spin speed of 4000 rpm). This is however also dependent also on the solvent used and the viscosity of the solution. The numbers given here are for solutions in which the propionic acid to butanol ratio is 2:3.

Different drying, pyrolysis and crystallization processes can lead to different microstructures of the final film. Microstructural differences can lead to differences in electrical and optical properties. The use of a two-step or one step method for crystallization depends also on the atmosphere, because usually when a reducing atmosphere is required a two step process is preferred. Therefore depending on the requirements of the final microstructure or atmosphere either single or multiple steps are implemented.
Chapter 3

Experimental procedures

In this chapter a brief description of the experimental procedures is given along with the characterization methods. First, details regarding preparation of the platinized wafers, followed by synthesis of the standard solutions and finally fabrication of capacitors. Methods of physical and electrical characterization along with the details of the instruments used have been provided.

3.1 Fabrication of wafers with different adhesion layers

In order to fabricate platinized silicon wafers a number of steps are required. The Si (100) wafer procured from the supplier usually has a native layer of SiO$_2$. This wafer is first oxidized further in order to get an oxide layer of about 450nm. If platinum is sputtered on top of this SiO$_2$ it does not adhere well. Therefore an adhesive layer, in this case of TiO$_2$ is deposited on top of this layer. About 10 nm Ti is sputtered on top of the SiO$_2$. This Ti layer is oxidized at 700°C in oxygen to convert it to TiO$_2$. 100nm of platinum is then sputtered on this layer at 150°C. These wafers, which are also available commercially with similar specifications, are stable till 800°C. Above 800°C the platinum layer forms hillocks and often the layer either peels off or the hillocks are so large that they penetrate through the film
Experimental procedure

surface and short the sample. In another set the adhesion layer was changed to AlO\textsubscript{x} instead of TiO\textsubscript{2}. The following SEM graphs show the platinum wafers annealed at 1000°C.

![SEM graphs of platinum wafers](image)

**Figure 3.1.1 (a)** TiO\textsubscript{2} adhesive layer 1000°C  **(b)** TiO\textsubscript{2} adhesive layer 1000°C  **(c)** AlO\textsubscript{x} adhesive layer 1000°C  **(d)** AlO\textsubscript{x} adhesive layer 1000°C.

From the above SEM pictures (fig. 3.1.1) we can see that with TiO\textsubscript{2} adhesive layer the Pt forms hillocks but with AlO\textsubscript{x} as an adhesive layer there are no hillocks. The reason for Pt on TiO\textsubscript{2} peeling off can be the phase transition (rutile to anastase) occurring above 800°C for TiO\textsubscript{2} resulting in compressive stress in the platinum layer, which is released by the formation of hillocks. In most of the experiments the more common Si/SiO\textsubscript{2}/TiO\textsubscript{2}/Pt wafers are used but when temperatures higher than 800°C are required for crystallization, Si/SiO\textsubscript{2}/AlO\textsubscript{x}/Pt wafers are used.

### 3.2 Preparation of solutions

**A-site substituted BT solution**

(Ba,Sr)TiO\textsubscript{3} solutions were prepared from barium propionate, strontium propionate and acetylacetone stabilized titanium \textit{n}-butoxide. At first, the propionates were derived by dissolving puratronic BaCO\textsubscript{3} (Alfa Aesar, puratronic) and SrCO\textsubscript{3} (Alfa Aesar, puratronic) in propionic acid. Acetylacetone was added to a solution of titanium butoxide in butanol. The preparation procedure is shown in figure 3.2.1. After, the chelation is complete (solution turns dark yellow or orange after sometime) this solution is added to the propionate solution. The molarity of the solution is adjusted by always keeping the propionic acid to butanol ration 2:3.
B-site substituted BT solution

A flowchart showing the preparation of the precursor solution is shown in Fig 3.2.2. The starting materials for the preparation of the solution were barium propionate, zirconium tetra-$n$-butoxide and titanium tetra-$n$-butoxide. The barium propionates are derived from the BaCO$_3$ (Alfa Aesar, puratroic). The zirconium tetra-$n$-butoxide (Alfa Aesar) and titanium tetra-$n$-butoxide (Alfa Aesar) were first dissolved in butanol and then 2 moles of acetylacetone were added to each of them. The Ba(Ti$_{1-X}$Zr$_X$)O$_3$ solutions with $X = 0.0, 0.1, 0.2, 0.3$ and $0.4$ were synthesized. For Hf-substituted BT films instead of the zirconium precursor, hafnium butoxide precursor was used. Ba(Ti$_{1-X}$Hf$_X$)O$_3$ solutions were made also with $X = 0.0, 0.1, 0.2, 0.3$ and $0.4$. 

![Flowchart for the preparation of BST solution](image)
Experimental procedure

3.3 Fabrication of capacitors

On platinized silicon substrates

Before the film is deposited the bare platinum substrate is annealed for 5 minutes in the RTA to relax any deposition-induced stress. Once the film is deposited and crystallized (diffusion oven / RTA), electrodes have to be deposited on top in order to characterize them in the metal-insulator-metal (MIM) form. In order to do so, first the films are covered with a negative photoresist layer. This photoresist layer is developed after exposure to UV light. Platinum is then sputtered on this developed resist layer and finally the undeveloped parts are dissolved out using acetone. The process is outlined schematically in figure 3.3.1.
After the deposition of the top electrodes the films are annealed at 700°C for 5 minutes in oxygen to ensure a better contact between the top electrode and surface. Without an electrode anneal, there are problems with higher leakages and shifted capacitance voltage curves.

**On nickel bottom electrodes**

Fig. 3.3.2 Setup for the processing of Ba-based perovskite dielectrics on nickel bottom electrodes. N₂/H₂ mixture is passed through water before introduction into the oven in order to equilibrate the partial pressure of oxygen.
Experimental procedure

For processing dielectric thin films with nickel bottom electrodes a diffusion oven was used with reducing atmosphere in order to prevent oxidation of the base metal electrodes. The tube could be moved in and out of the furnace manually (fig. 3.3.2). Temperatures were preset in the furnace to the required value and then the tube moved out towards the left. Once the substrates were placed inside the tube, it was flushed with N₂/H₂ mixture for 5 minutes before moving the tube to the hotzone of the furnace. After the crystallization period, the tube is again moved out and the temperature is allowed to reduce for an hour before the substrates are removed. After the required number of coating and crystallization steps top electrodes of Ni+Au were deposited.

3.4 Physical characterization methods

X-Ray diffraction

In order to check for the crystallographic texture of the deposited films, X-ray diffraction measurements were performed using an X’PERT diffractometer (Phillips) with CuKα radiation. The diffractometer was used both in glancing angle incident x-ray diffraction (GIXRD) mode and also in the θ-2θ mode figure 3.4.1(a). For most of the thin films the GIXRD mode was used during which the incident beam was fixed at a small angle, usually 1°.
or less. In this mode the penetration depth of the thin film is more and therefore is more sensitive to the presence of any secondary phases Figure 3.4.1(b).

**Scanning electron microscopy**

Scanning Electron Microscopy (SEM) was performed with a Gemini 982. SEM was performed on most films to understand the microstructure and morphology of the films as a function of different processing parameters. Both cross sectional and surface scans were performed for the films. Thickness of the films and also grain size were at times verified with the SEM. In the following figures a typical cross sectional and surface SEM scan is shown.

![Cross sectional micrograph of a sample.](image) ![Surface micrograph of a sample](image)

**Figure 3.4.2(a)** Cross sectional micrograph of a sample. **(b)** Surface micrograph of a sample

**UV-VIS &-FT-IR spectroscopy**

FT-IR- spectroscopy was performed with a Mattson Genesis spectrophotometer equipped to measure the spectra in the reflectance mode. Detection of residual carbonate phases for films deposited at different temperatures was done with FT-IR. UV-VIS spectrophotometer was used for measuring the transmission spectra of the films deposited on quartz substrates. From the transmission spectra it was possible to derive the band gap, refractive index and the extinction coefficient of the films.
Experimental procedure

Figure 3.4.3.(a) FT-IR of a BST film crystallized at 650°C showing the presence of carbonates and also the Ti-O vibration. (b) Transmission spectra of BT film on quartz substrate.

**DTA-TGA**

Relative thermo gravimetric analysis and differential thermal analysis of the solution were performed in order to gain an insight into their decomposition behavior. Analysis of the decomposition behavior gives an idea about the temperatures at which the amorphous material becomes organic free.

**3.5 Electrical characterization methods**

Temperature dependent dielectric studies were performed using an impedance analyzer (HP4294A). A Keithley 617 programmable electrometer was used to measure the current response of the samples while doing $I-V$ measurements. Depending on the type of measurement required the impedance analyzer or the electrometer was attached to the probe station. The temperature of the probe station was controlled using a Eurotherm temperature controller. Both the impedance analyzer and the electrometer could be controlled via an IEEE488 bus interfaced with a computer.

The current voltage characteristics ($I-V$) were measured as functions of temperature and applied voltage. When a voltage is applied to a dielectric, the current response is
composed of a polarization contribution and a leakage contribution. This distinction is important because a voltage step method was employed in determining the \( I-V \) characteristics. For this method a voltage is applied to the films and the current is measured only after a certain period of time \( \tau \) has elapsed (Figure 3.5.1). At times less than some crossover time this current is dominated by displacement current while at longer times it is dominated by the true leakage. But care should be taken so that the step time period does not reach the degradation regime of the sample.

![Diagram](image.png)
Chapter 4

Perovskite thin films

Perovskite materials display a wide range of properties that make them attractive for a variety of electronic ceramic applications. The structure is named from the naturally occurring mineral perovskite (CaTiO$_3$)$^{45,46}$. Perovskites are usually depicted in a pseudocubic form as shown in figure 4.1. The structure contains two cation sites in the lattice: the larger cation A is on the corners of the cell while the smaller cation is at the centre of the unit cell. The O ions are situated at the centre of the faces, thereby forming a network of corner linked oxygen octahedra, with the larger cation (A) filling the dodecahedral holes and the smaller cation (B) filling the octahedral sites.

Fig. 4.1. Structure of tetragonal ABO$_3$ perovskite cell.
In most cases the above picture is somewhat idealized. In fact, any structure consisting of the corner-linked oxygen octahedral with a small cation filling the octahedral hole and a large cation (if present) filling the dodecahedral hole is usually regarded as a perovskite, even if the oxygen octahedral is slightly distorted. The anion need not be oxygen, it can be fluoride, chloride, hydride, and sulphides. A wide variety of cations can be substituted in the perovskite structure. The relationship (Goldschmidt tolerance factor)

\[ t = \frac{R_A + R_O}{\sqrt{2(R_B + R_O)}} \]  

(1)

describes the ideal cubic perovskite structure where \( t = 1.0 \) and \( R_A, R_B \) and \( R_O \) indicate the ionic radius of large cation, small cation and anion respectively. In practice, those structures whose tolerance factor \( t \) is about 0.95-1.0 are cubic, those with lower values are slightly distorted but non-ferroelectric and those slightly over 1.0 tend to be ferroelectric. Polarizability of the ions has also been shown to be an influential parameter. At least one more factor should be considered in this ‘hard sphere’ model of ions in contact: the fact that bonding is not necessarily ionic. The approach gives a good general picture of what to expect in the perovskite structure. However the Goldschmidt tolerance factor does not apply to perovskites with numerous ion vacancies.

Perovskites are often divided into different classes depending on the valency of the A and B site cations. Examples include BaTiO\(_3\), NdAlO\(_3\), complex perovskites like Pb(Mg\(_{1/3}\),Nb\(_{2/3}\))O\(_3\) and layered perovskites like SrBi\(_2\)Ta\(_2\)O\(_9\): Other technologically important perovskites include Pb(Zr,Ti)O\(_3\), SrTiO\(_3\), (Ba,Sr)TiO\(_3\), (La,Sr)CoO\(_3\) and YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\).

While the perovskite structure is usually depicted in pseudocubic form, slight distortions from cubic symmetry are responsible for most of the interesting properties of these materials. For BaTiO\(_3\) these properties are a direct result of the displacement of the B-site species (Ti) from the centre of the unit cell, resulting in the tetragonal, rhombohedral or
Perovskites

orthorhombic symmetry. For PZT, Warren et.al. have shown that in addition to the Zr and Ti displacement, displacements of the A-site species also contribute to ferroelectric behaviour.

4.1 Ferroelectric perovskite materials

Ferroelectric materials are those materials in which the spontaneous electric polarization can be reoriented between crystallographically defined states by an external electric field. The ability of a crystal to exhibit spontaneous polarization is related to its symmetry. Of 32 point groups, which describe all crystalline systems, 11 are centrosymmetric and contain an inversion center. In such structures, polar properties are not possible because any polar vector can be inverted by an existing symmetry transformation. Of the remaining 21 point groups without an inversion center, 20 can show piezoelectricity. A further subdivision may be made, consisting of those 10 crystal classes, which contain a unique polar axis (an electric dipole moment) in the unstrained condition. Such crystals may exhibit spontaneous polarization parallel to the polar axis. In its tetragonal phase, BaTiO$_3$ is such a material. In the cubic phase of BaTiO$_3$, the central Ti atom serves as an inversion center making spontaneous polarization impossible. With the occurrence of a tetragonal deformation, the positively charged Ba and Ti ions are displaced with respect to the negatively charged O ions, thereby creating a polar axis in the direction of the tetragonal deformation, which marks the direction of the spontaneous polarization. Thus it is not only the existence of spontaneous polarization, but its reorientability by an external field, which defines a ferroelectric material.

Since the discovery of the usefulness of BT, an enormous effort has been made to study the properties of compositionally modified ceramic bodies. The partial substitution of Ba with Sr causes the Curie temperature, as well as the lower transition temperatures to decrease. Sr is smaller than Ba and consequently it provides less ‘rattling’ space for Ti. Similar effects were found by replacing Ti by Zr or Sn. Both Zr and Sn are larger than Ti, so
that the substitution decreases the total volume available to the ‘rattling’ Ti. However packing alone cannot explain the results in all systems; since in solid solutions of (Pb,Ba)TiO$_3$ the Curie point was found to increase with increase of Pb concentration though Pb is smaller than Ba. Other factors like polarizability and the character of the bonding must be taken into account. Most of the compositions were studied for MLCC or surface mounted device applications, which required ceramic powders. However the properties of all these materials have not been studied in thin film form. Therefore it is of great interest to study the property of some of these compositions in thin film form, in view of future applications. When a material is deposited in thin film form its properties can vary largely due to substrate effects, processing temperatures and deposition methods. In the following sections both A-site and B-site substituted BT will be studied in terms of their dielectric and leakage properties.

4.2 Optimization of film deposition parameters

A co-relation between processing and final device characteristics is of utmost importance. Differences in microstructure and electrical properties were observed when chemical solution deposited thin films were annealed using a conventional diffusion furnace, rapid thermal annealing furnace with different heating ramps, and a hot plate for pyrolysis prior crystallization. Therefore before we deposit barium based perovskite thin films it is important to optimize some parameters, which lead to acceptable film properties$^{49}$. 

The films of composition (Ba$_{0.7}$Sr$_{0.3}$)TiO$_3$ were deposited on Pt coated Si substrates by a 0.1M solution. The details for the preparation of the precursor solution have been provided previously in section 3.2. The films were crystallized in three different ways. A flowchart depicting the different procedures for annealing the films is shown in figure 4.2.1 In the first method the films were dried and pyrolysed at 200$^\circ$C and 400$^\circ$C and then after the desired
Perovskites

thickness was reached, it was crystallized at 700°C for 30 minutes (two-step process). In the second method the films were directly crystallized in the RTA for 10 minutes. The ramp rate was varied in the RTA and it was found that when the ramp rate was set to around 80 °C/sec the films attained a columnar structure. Faster ramp rates of about 160 °C/sec yielded non-columnar grains and a lower dielectric constant. Finally in the third method the films were crystallized in the diffusion furnace. The second and the third methods have no intermediate drying and pyrolysis steps (one-step process). The cross-sections of the films were then examined using a SEM. The electrical properties were studied after depositing Pt top electrodes, which had been structured with a lift-off process.

![Figure 4.2.1](https://example.com/flowchart.png)

**Figure 4.2.1** Flowchart depicting the different crystallization methods applied on the thin films.

To study the structural differences of the films processed by the three different ways cross-sectional SEM’s were performed on the films. The films which were dried and pyrolysed at 200 and 400°C respectively and then crystallized at the end after the desired
thickness (about 200nm) was achieved showed a coarse grain structure (Fig. 4.2.2.a). The reason for such a microstructure can be explained easily. Since the films were coated repeatedly after the pyrolysis, a thick amorphous layer was achieved at the end of all the coatings and when this was heated in the diffusion furnace at 700°C homogeneous nucleation was predominant. Cross sectional SEM pictures of the films are shown below.

![Fig. 4.2.2.a](image1)
![Fig. 4.2.2.b](image2)
![Fig. 4.2.2.c](image3)
![Fig. 4.2.2.d](image4)

**Fig. 4.2.2.(a)** Hot Plate pyrolysis and then crystallized in the diffusion furnace **(b)** RTA processed with a ramp rate of 160 °C / sec **(c)** RTA processed with a ramp rate of 80 °C / sec **(d)** Diffusion furnace crystallized.

The columnar grain growth with lower concentration can be explained with the help of the model proposed by Gust et. al.\textsuperscript{50}. For BST the initial nucleation takes place throughout the amorphous mass (homogeneous nucleation) unlike PZT where the nucleation is predominantly at the interface between the crystalline Pt bottom electrode and the amorphous...
Perovskites phase (heterogeneous nucleation). This leads to perfectly columnar structured grains in PZT even with higher concentrated solutions (typically ~ 0.5 M). With BST this is not possible, hence the solution concentration is decreased\(^6\) and the thickness of the amorphous layer is reduced thereby forcing the nucleation to take place at the interface of the bottom electrode and the amorphous layer. Therefore films crystallized in the diffusion furnace directly after deposition possesses columnar structure (fig. 4.2.2.d). However, in the RTA with faster ramp rates (160 °C / sec), even with the low concentration precursor solutions (0.1M) it was not possible to get columnar grains. The reason for this could be the extremely fast ramp rate which caused the BST to nucleate somewhat homogeneously. So the ramp rate was reduced to 80 °C / sec and this yielded columnar grained BST films with electrical properties comparable to those produced in the diffusion furnace directly (fig. 4.2.2.c). On the basis of the model by Schwartz et.al\(^{51}\) this can be explained. Slower heating rates yielded films with columnar microstructures dictated by a single interface nucleation effect, whereas faster heating rates, allow less time for growth of the initially nucleated grains, display both heterogeneous and homogeneous nucleation. For these films because of the faster heating rate, the energy barrier for homogeneous nucleation is surmounted prior to the completion of the transformation via

![Figure 4.2.3](image)

**Figure 4.2.3.** Hypothetical relationship between heating rate used during the crystallization heat treatment and the free energy barriers for heterogeneous and homogeneous nucleation. Heating time \(t_1 < t_2 < t_3\).
the initial nucleation event, and therefore the resultant microstructure is defined by multiple nucleation events. This has been represented in fig. 4.2.3. Hence, films which were crystallized in the RTA with very high heating ramps (160°C/sec) were found to be non-columnar. Film thickness effects are also expected to play a part in the final microstructure due to the change in the time required for the growth of the interface nucleated grains to consume the amorphous film. Therefore in the first method where repeated pyrolysis steps were performed before a final crystallization homogeneous nucleation was observed. The amorphous film thickness was too large to favour heterogeneous nucleation thereby leading to a non-columnar structure in the films (fig. 4.2.2.a).

In order to study the electrical properties of the films crystallized by the three different methods described previously (Fig. 4.2.1), top electrodes of platinum were deposited by a photolithographic lift-off process as described in chapter 3. Before electrical characterization, the films were annealed for 5 minutes in the RTA at 700°C to ensure better contact between the top electrodes and the surface of the BST thin films. In figure 4.2.4 the dielectric dispersion of the three different films is shown. It is observed that the dielectric constant remains almost constant for the entire frequency spectrum between 1 kHz and 1 MHz. The columnar films have higher dielectric constant as compared to the small grained films. Also,

![Figure 4.2.4](image)

**Figure 4.2.4** Dielectric constant versus frequency from 1kHz to 1MHz of the three different types of films. Columnar films have higher dielectric constant.
Perovskites

The direct diffusion oven crystallized films have less frequency dispersion with reference to the others. The dielectric constant versus voltage plots for the different films is shown in figure 4.2.5.a, 4.2.6.a, and 4.2.7.a. A small alternating current signal of 50 mV amplitude was applied while the dc electric field was swept from positive bias to negative bias. The tunability of each type of film was calculated with the following equation

\[
\text{Tunability} = \frac{\varepsilon_{\text{max}} - \varepsilon_{\text{min}}}{\varepsilon_{\text{max}}}
\]

The films crystallized in the RTA with the lower heating ramp (80 °C / sec) were found to have the greatest tunability with 41%, followed by the films crystallized in the diffusion furnace with 39%, and the films dried and pyrolyzed on the hot plate and then crystallized in the diffusion furnace (two step process) at the end showed only a tunability of 27%.

![Dielectric constant versus voltage at different Frequencies](image1.png)

![Current density versus electric field at different temperatures for hot plate processed films](image2.png)

![Dielectric constant versus voltage for different temperatures](image3.png)

![Current density versus electric field for different temperatures](image4.png)

**Fig. 4.2.5. (a)** Dielectric constant versus voltage at different Frequencies. **(b)** Current density versus electric field at different temperatures for hot plate processed films.
The current voltage characteristics \((I-V)\) were measured as functions of temperature and applied voltage. When a voltage is applied to a dielectric, the current response is composed of a polarization contribution and a leakage contribution. This distinction is important because a voltage step method was employed in determining the \(I-V\) characteristics. For this method a voltage is applied to the films and the current is measured only after a certain period of time \(\tau\) has elapsed. At times less than some crossover time this current is dominated by displacement current while at longer times it is dominated by the true leakage.

The basic conduction mechanisms in insulating films can be classified into electrode-limited or bulk limited conduction. In Pt/BST/Pt capacitors the main current conduction mechanisms are electrode limited, i.e. either Schottky emission or Fowler-Nordheim tunnelling, or a combination of both. To determine whether the operating mechanism controlling the leakage is really Schottky it is essential to investigate both the field dependence and the temperature dependence of the leakage current. The Schottky equation is as follows
The leakage current characteristics for the three different films at different temperatures are presented in a log \((J)\) versus \(E\) plot in figure 4.2.7.b, 4.2.7.b, and 4.2.7.b.

![Figure 4.2.8. A plot of \(\ln J/T^2\) versus \(1000/T\) for differently processed BST thin films.](image)

The \(\ln J/T^2\) versus \(1000/T\) plots is shown in the figure 4.2.8. The RTA and the direct diffusion furnace processed films show a linear behaviour as expected if the conducting mechanism is indeed Schottky. Plots of \(\ln J\) versus \(E/\) were also linear. The barrier heights were calculated for both types of films and found to be around 1.1eV. Similar values had been reported previously by Dietz et. al.\(^{55}\). The films, which were pyrolysed and then annealed could not be explained with the help of Schottky theory.

The dielectric constant of the films was found to be highest when the films were directly processed in the diffusion furnace. This was due to the almost perfectly columnar structure of the grains. These films showed smaller dielectric dispersion. The leakage properties of the films were also studied and it was noticed that the films processed in the RTA (with lower heating ramp) and directly in the diffusion furnace show lower leakage as compared to the films, which were made with an intermediate pyrolysis step in the hot plate.
and then annealed in the diffusion furnace. Since the films processed in the diffusion oven have the best dielectric properties, lowest frequency dispersion and low leakage, all films deposited hereafter are directly crystallized in the diffusion oven unless specifically mentioned.

### 4.3 A-site substituted BaTiO$_3$ : (Ba,Sr)TiO$_3$

Research involving barium strontium titanate thin films((Ba,Sr)TiO$_3$) started mainly because in the early 1990’s it was envisaged that in order to make devices smaller and to keep in tandem with Moores law, new high dielectric constant materials would be required. The semiconductor industry has till date managed to use other dielectric materials and different device geometries to meet its requirements. However, BST based dielectrics are now potential candidates for phase shifters and other tunable microwave devices.

The Curie point of BaTiO$_3$ decreases linearly with the addition of strontium (figure 4.3.1.a). The shift in the transition temperatures with addition of Sr, for ceramics, is shown in the figure below. For thin films the phase transitions are not so prominent and depend greatly on the thickness of the films. The phase transition temperature is greatly dependent on the substrate used$^{56}$, thickness of the films$^{57}$ (figure 4.3.1.b) and even the top electrodes$^{58}$.

![Figure 4.3.1 Phase transition with (a) various Sr concentrations in ceramics and (b) for (Ba$_{0.75}$Sr$_{0.25}$)TiO$_3$ thin films with different thicknesses.](image)
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**Characterization of (Ba, Sr)TiO$_3$ thin films**

For the columnar films a 0.1M solution was used and for polycrystalline films 0.3M solution was used. The details of the synthesis procedure are given in chapter 3. For most of the dielectric and electrical characterizations usually 0.1M solutions were used which led to columnar films with higher dielectric constant.

Scanning electron microscopy performed on the films revealed the columnar structure of the films (figure 4.3.2). All films were derived from 0.1M solution. With increase of Sr content the grain size laterally is found to increase slightly.

![Cross-sectional SEM pictures](image)

**Figure 4.3.2** Cross-sectional SEM pictures of (a) (Ba$_{0.9}$Sr$_{0.1}$)TiO$_3$ (b) (Ba$_{0.7}$Sr$_{0.3}$)TiO$_3$ (c) (Ba$_{0.5}$Sr$_{0.5}$)TiO$_3$.

The capacitance of the films as a function of voltage was measured for the three compositions at different temperatures of crystallization. Average dielectric constant was calculated from the capacitance (figure 4.3.3). It was noticed that for all the compositions there was a large increase of dielectric constant when the films were annealed above 600$^\circ$C. As reported by various other groups BT and substituted BT thin films when derived by
normal CSD methods always crystallize above 600°C. This had been attributed to the formation of oxo-carbonate intermediate phases, which decompose only above 600°C. Annealing at still higher temperatures yields films with higher dielectric constant, probably due to further removal of organic moieties and pores. For ceramics, usually temperatures of around 1250 - 1350°C are used. But these temperatures are not feasible with normal semiconductor processing. The platinised silicon substrates which are normally used for most dielectric thin film deposition and characterization in MIM form are stable till 750°C. Tunability of the films at 7 volts for the films are 55.5 %, 50% and 38% for the (Ba_{0.9}Sr_{0.1})TiO_3, (Ba_{0.7}Sr_{0.3})TiO_3, (Ba_{0.5}Sr_{0.5})TiO_3 thin films respectively.
Figure 4.3.4. The frequency dispersion of the three different composition is shown at two different temperatures. The filled symbols are for films deposited at 700°C and the open symbols are films deposited at 600°C.

Frequency dispersion of the films is shown in the figure 4.3.4. Films deposited at 700°C show less frequency dispersion as compared to films deposited at 600°C. This could be due to the higher crystallinity and phase purity of the films deposited at higher temperatures.

4.4 B-site substituted BaTiO$_3$: Ba(Zr,Ti)O$_3$ and Ba(Hf,Ti)O$_3$

An example of B site substituted BaTiO$_3$ is Ba(Ti$_{1-X}$Zr$_X$)O$_3$, which have been used as a dielectric material in multi-layer ceramic capacitors (MLCC's) for the past few decades. Depending on the amount of zirconium (Zr) substitution in (BaTiO$_3$) it behaves as a ferroelectric or a relaxor$^{59}$. A partial substitution of Ti by Zr, Hf or Sn leads to a decrease of the Curie point accompanied with a reduced $c/a$ ratio and decrease in spontaneous polarization$^{60}$. For ceramics it has been noticed that the phase transition changes from first order to second order for Zr content $\geq$13 atomic % and for 27 atomic % or more the phase transition becomes diffuse and relaxor like$^{61}$. Recently there has been a great interest in lead free relaxors like Zr substituted BaTiO$_3$. Gui$^{62}$ had performed TEM studies on films of BT substituted with Zr. Therefore a comprehensive study with Zr substitution was performed$^{63}$. 

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Another interesting substitution element would be hafnium (Hf). Though there are some reports of Hf substituted BT ceramics, thin films of Ba(Hf,Ti)O$_3$ have not been studied. HfO$_2$ is now being considered for the next generation of gate dielectrics due to its better leakage properties. Therefore it is of interest to see the effect of Hf substitution on the electrical properties of Hf substituted BT thin films$^{64}$.

**Structural characterization of Ba(Ti,Zr)O$_3$ and Ba(Ti,Hf)O$_3$ thin films**

The crystalline nature of the thin films was identified by glancing angle X-ray diffraction (XRD). This helped to eliminate the substrate reflections. The XRD patterns were recorded with a CuK$_\alpha$ radiation at 45kV. Fig. 4.4.1.a and 4.4.1.b shows the XRD patterns of the different Zr and Hf substituted BT thin films. It is a known fact that with increase of Zr content the lattice size increases since the Zr ionic radius (79pm) being greater than the Ti ionic radius (68 pm). The grain size of the films were calculated from the Scherrer equation given below (Eq.2)

$$t = \frac{0.9\lambda}{B\cos\theta}$$  \hspace{1cm} (4.3)

where, $t$= crystallite thickness, $\lambda$= X-ray wavelength, $B$=Full Width at Half Maximum (FWHM) of the peak. The broadening due to strain and instrument were neglected during the

![Figure 4.4.1.](image-url)
Perovskites

calculation of the crystallite size. The grain size was found to be around 60nm for the undoped BT thin films. It was found to reduce with increase of Zr substitution. This could be due to the larger size of the Zr ion, which hinders the grain growth rate due to its slower diffusion rate. This can be supported by a related but different study of Sr substituted BT, where grain growth is observed with larger amounts of Sr substitution\textsuperscript{65}. Sr ion has a smaller ionic radius compared to Ba ion and thus leads to fast diffusion and grain growth. Also, worth noticing is the shift of the (110) peak to lower $\theta$ values, indicating an increase in the lattice parameters with Zr/Hf substitution (fig. 4.4.2.a and fig. 4.4.3.a). From the position of the 110 peaks the lattice parameters are calculated for both the Zr and the Hf substituted BT films. The lattice parameters are calculated assuming a pseudocubic structure. With higher and higher Zr/Hf

![Graph](image1)

**Figure 4.4.2 (a)** Shift of the (110) peak with increased Zr substitution, indicating an increase in the lattice constants. **(b)** Lattice constant of the different compositions.

![Graph](image2)

**Figure 4.4.3 (a)** Shift of the (110) peak with increased Hf substitution, indicating an increase in the lattice constants. **(b)** Lattice constant of the different compositions.
substitution the lattice parameter increases. The cross-sectional SEM's support the above stated fact that grain size reduces with higher amounts of Zr substitution. Fig. 4.4.4 shows the cross-sectional SEM of the different Zr substituted films. The films were crack free and dense. All the films were of similar thickness of around 400nm. These films were derived from 0.3M solution. Sometimes in higher Zr or Hf substituted BT thin films (derived from 0.3M solution), apparently the films seem to be columnar but on a closer look the finer grains become visible.

**Figure 4.4.4** Cross sectional SEM of different Zr substituted thin films annealed at 700°C. The grain size is found to decrease with higher and higher Zr substitution.

For Hf-substituted BT thin films both the 0.1M solution and 0.3M solution derived film microstructures are analyzed. For the 0.1M solution films as opposed to BST thin films higher Hf substitutions lead to loss of columnar structure. Whereas for the 0.3M solution films the grain size is found to decrease continuously. A closer look at the BHT40 (0.3M) shows the fine grain structure of the films but apparently they appear to be columnar.
Figures 4.4.5 (a), (c), (e), (g) Different BHT films derived from 0.1M concentration.
Figures 4.4.5 (b), (d), (f), (h) Different BHT films derived from 0.3M concentration.
Electrical characterization of the Ba(Ti,Zr)O$_3$ thin films

The polarization hysteresis of the films as shown in Fig. 4.4.6 was measured with a ferroelectric test system. The hysteresis loops became slimmer with larger amounts of Zr substitution. At this point it might be stated that the typical hysteresis with large remnant polarization, which is expected for ferroelectric BT, is absent in our case. This could be due to the strain at the film substrate interface. Pertsev et.al. had shown this theoretically with thermodynamic theory.

Figure 4.4.6 Polarization hysteresis of the different Zr substituted BT thin films.

Figure 4.4.7 Dielectric constant versus voltage of the different Zr substituted BT thin films.
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Dielectric properties

The average dielectric constant versus voltage measurement is shown in Fig. 4.4.7. It was found that for higher Zr substitutions the average dielectric constant decreased. However for a Zr substitution 10% the dielectric constant had increased. Similar observations had been made for ceramics.

![Dielectric Constant vs Frequency](image1)

**Figure 4.4.8** Frequency dispersion of dielectric constant and loss tangent of the different Zr substituted BT thin films.

Fig. 4.4.8 shows the frequency domain response of the Zr substituted BT thin films. The dielectric constant for all the films shows little dispersion within the measured frequency range. This is because the measurements were performed at room temperature and with increase in Zr substitution the $T_C$ shifted to lower temperatures. The phase transitions of the various films have been shown in Fig. 4.4.9(a-e). With increase of Zr substitution the dielectric constant was found to decrease after an initial increase and the transition temperature was also found to shift towards lower temperatures. The phase transitions were measured at three different frequencies. For ceramics, Hennings *et al.* noticed that on increasing Zr content the transition between phases in BT converge, to a single point with composition $x \geq 0.1$. All the phase transitions were noticed to be diffused in nature and the reason for this could be attributed to the small grain size in thin films. Later it will be shown...
that dielectric constant and phase transition behavior is also dependent on the crystallization temperature.

**Figure 4.4.9.** Phase transition of (a) 0 percent Zr substituted (BTZ0) (b) 10 percent Zr substituted (BTZ10) (c) 20 percent Zr substituted (BTZ20) (d) 30 percent Zr substituted (BTZ30) (e) 40 percent Zr substituted thin films (BTZ40).
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In classical relaxors, strong frequency dispersion is observed at the low temperature slope of the peak, while the high temperature slope is independent of frequency, so that the position of the \( T_m \) shifts to lower temperatures with decreasing frequency, satisfying the Vogel-Fulcher relationship\(^{67} \). There are mainly two methods, which have been widely used in research on the relaxor ferroelectrics, to characterize it. The first one is a quadratic relationship; given by Smolensky\(^{68} \) and the second which is a power law relation has been given by Burfoot\(^ {69} \). The power law relationship as given by Burfoot is as follows:

\[
\frac{\varepsilon_m}{\varepsilon} = 1 + \frac{(T - T_m)^\gamma}{2\delta^2}
\] (4.4)

Here \( \varepsilon_m \) is the maximum value of the dielectric constant and \( T_m \) is the temperature at which the maximum dielectric constant is attained. When \( \gamma = 1 \) the above equation expresses the Curie-Weiss behavior of the ferroelectrics, while for \( \gamma = 2 \) it reduces to the one given by Smolensky. The \( \delta \) and \( \gamma \) are constants. The value of \( \gamma \) (\( 1 \leq \gamma \leq 2 \)) is the expression of the degree of dielectric relaxation in a relaxor ferroelectric. Figure 4.4.10 shows the plot of \( \ln(\varepsilon_m/\varepsilon - 1) \) versus the \( (T - T_m) \) plot. The value of \( \gamma \) was calculated from the slope of the plot of \( \ln(\varepsilon_m/\varepsilon - 1) \) versus \( \ln(T - T_m) \) and is shown in table 1 as a function of Zr substitution. It is noticed that wither higher amount of Zr substitution (Zr substitution 30% or more) the \( \gamma \) values have a value \( \approx 2 \) which represent ideal relaxor ferroelectrics\(^{70,71} \).

<table>
<thead>
<tr>
<th>Zr%</th>
<th>( \gamma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.001</td>
</tr>
<tr>
<td>10</td>
<td>1.466</td>
</tr>
<tr>
<td>20</td>
<td>1.749</td>
</tr>
<tr>
<td>30</td>
<td>2.090</td>
</tr>
<tr>
<td>40</td>
<td>2.051</td>
</tr>
</tbody>
</table>

\( \gamma \) values of the different BTZ thin films

Figure 4.4.10. Plot of \( \ln(\varepsilon_m/\varepsilon - 1) \) versus \( \ln(T - T_m) \) at 10 kHz for the different BTZ films
I-v characteristics

The results of leakage current measurements at a particular temperature for the different films are shown in figure 4.4.11. When a voltage is applied to a dielectric, the current response is composed of a polarization contribution and a leakage contribution. This distinction is important because a voltage step method was employed in determining the I-V characteristics. The basic conduction mechanisms in insulating films can be classified into electrode-limited or bulk limited conduction. In Pt/BST/Pt capacitors the main current conduction mechanisms are electrode limited, i.e. either Schottky emission or Fowler-Nordheim tunneling, or a combination of both.

![Figure 4.4.11. Plot of Log J versus E for the different BTZ films.](image)

Figure 4.4.11 shows the leakage versus field measurements for the different films. The leakage was found to have increased with a Zr substitution of 10% and then decreased again till a Zr substitution of 40%. The most favored mechanism to investigate is the Schottky barrier limited current flow. In this case the charge carriers are thermally excited over an energy barrier at the metal-ceramic interface. This barrier is created by the equilibration of charge carriers in the ceramic thin film and the electrode, and its value at zero electric field is modified by a field dependent barrier lowering. This barrier lowering is due to the image
Perovskites forces\textsuperscript{76}. To determine if this is the operant mechanism it is necessary to investigate both the field and temperature dependence of the leakage current. The current density for a Schottky diode is given by equation 4.2. A plot of ln $J$ versus $E^{1/2}$ is shown in figure 4.4.12.a. It was noticed that in the high field region there was a linear relationship between them. This is expected if the leakage current obeys the Schottky conduction mechanism. The barrier height $q\Phi_B$ and the Richardson constant ($A^*$) can be calculated from the slope and the ordinate of the plot of ln $J/T^2$ versus $1000/T$ (figure 4.4.12.b). The linear region becomes prominent only when the leakage measurements are performed at higher temperatures.

![Graph](image)

**Figure 4.4.12.** Plot of (a) ln $J$ versus $E^{1/2}$ for the different BTZ films (b) ln $J/T^2$ versus $1000/T$ for the different BTZ films at 10V.

The values of the barrier height are found to vary between 1.19 and 1.15 eV. Scott \textit{et al.}\textsuperscript{77} had reported the barrier heights for strontium substituted BT thin films to be around 1.6 eV.

**Electrical characterization of Ba(Hf,Ti)O\textsubscript{3} thin films**

**Dielectric properties**

Dielectric constant of the films was measured as a function of the voltage for both sets of films (fig 4.3.13). The measurement was performed by superimposing an ac signal of
100mV at 10kHz with dc bias on the films. It was found that with higher Hf concentrations the dielectric constant decreased. This is due to the fact that with increase of Hf substitution, the ferroelectric to paraelectric to phase transition shifts towards lower temperature. Here for comparison dielectric properties of films derived from both 0.3M solution and 0.1M solution are shown. The dielectric constant for the films derived from 0.3M solution are always lesser than the 0.1M films till 20% Hf substitution. But, more than 20 % Hf substitution leads to loss of the columnar structure even when the films are derived from 0.1 M solution. At this stage the dielectric constant becomes comparable for both types of films.

**Figure 4.4.13.(a)** Dielectric constant of the films derived from 0.1M solution concentration.  **(b)** Dielectric constant of the films derived from 0.3M concentration.

**Figures 4.4.14.(a)** Tunability of the different films measured as a function of temperature  **(b)** Frequency dispersion of the different films.
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Also the dielectric loss factor decreases with higher hafnium concentrations. The tunability of the films is found to decrease both with temperature and higher hafnium substitutions as can be seen from the figure 4.4.14.a. The frequency domain response of the different hafnium substituted films is shown in figure 4.4.14.b. Dielectric constant of all the films except BHT0 shows little dispersion within the frequency range of 100Hz to 1MHz.

I-V characteristics

The dc leakage currents were evaluated using a step voltage technique\textsuperscript{78}. For this technique a voltage is applied to the capacitor and the current is measured as a function of time. Correct procedure requires that a sufficient charging time is used to reach the steady-state dc leakage regime. The IV characteristic is then constructed from the true dc leakage data obtained from a series of such \( I-t \) measurements. It was noticed that 10 seconds was sufficient to avoid any polarization contribution to the leakage current.

The basic conduction mechanisms in insulating films can be grouped into either electrode limiting or bulk limiting. In most Pt/perovskite/Pt systems the main current conduction mechanisms are electrode limited, i.e. either Schottky emission or Fowler-Nordheim tunneling, or a combination of both\textsuperscript{79}. Therefore a series of I-V measurements at

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figures4415.png}
\caption{Current voltage characteristic of the BHT films at 150\textdegree C}
\end{figure}
different temperatures was taken for the 5 different compositions. In figure 4.4.15 the leakage of the different films at 150°C is shown. It is noticed that the leakage of the films decrease with increase of hafnium concentration. The most favored mechanism to investigate is the Schottky barrier limited current flow. To determine that this is indeed the operating mechanism it is necessary to investigate both the field dependence and the temperature dependence of the leakage current.

![Figure 4.4.16. (a) Plot of Ln $J$ versus $E^{1/2}$](image1)

![Figure 4.4.16. (b) Plot of Ln $J/T^2$ versus 1000/T](image2)

A plot of $\ln J$ versus $E^{1/2}$ is shown in figure 4.4.16.a. It was noticed that there was a linear relationship between them. This is expected if the leakage current obeys the Schottky formalism. The value of $\alpha$ is extracted from the slope and then together with the slope of the plot of $\ln J/T^2$ versus $1000/T$ (Figure 4.4.16.b) the barrier heights are extracted. The barrier heights are 1.05, 1.27, 1.29, 1.41 and 1.45 eV for BHT0, BHT10, BHT20, BHT30, BHT40 respectively. The decrease in leakage current can be attributed to this increase in the Schottky barrier height.

**Optical properties**
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The optical transmission spectra were recorded for the different samples in the wavelength range 200-800nm on fused silica. All the films were similarly processed as mentioned previously. Figure 4.4.17 shows the transmission spectra for BHT0 on quartz substrates. There is strong attenuation in the short wavelength region while there is strong interference oscillation in the long wavelength region.

![Transmission spectra of BHT films deposited on quartz glass substrates. Inset shows the refractive index of the films calculated from the transmission spectra.](image)

Tables 4.3.17. Transmission spectra of Bt films deposited on quartz glass substrates. Inset shows the refractive index of the films calculated from the transmission spectra.

The optical band gap ($E_g$) for the film was calculated by considering a direct transition between the valence and conduction bands on absorption of a photo of energy $hν$. In such a case the absorption coefficient $α$ is related to the band gap energy by the following equation

$$(α hν)^2 = C(hν-E_g) \quad (4.5)$$

Exponential variation of the transmittance ($T$) with absorption coefficient is more pronounced near the absorption edge. Hence the absorption coefficient can be determined from the following equation

$$T = A \exp(-αd) \quad (4.6)$$

where,

$$A = \frac{16n_e n_o (n^2 + k^2)}{[(n_e + n)^2 + k^2][(n_s + n)^2 + k^2]}$$
and \( n, n_0, n_s \) are the refractive indexes of the film, air and substrate respectively and \( k \) is the extinction coefficient of the film and \( d \) is the thickness. \( A \) is found to be unity at the absorption edge. \( E_g \) was calculated by using equation 4.5. In the low wavelength region \((\alpha h\nu)^2\) varied linearly with \( h\nu \). This straight-line behavior is observed if there is a direct band gap. For barium titanate and strontium titanate band gap calculations by this method have yielded quite accurate results. And, in fact BHT0 in our case, which is barium titanate, has a band gap of 3.6 eV which is similar to that reported by other groups previously. With increase of Hf substitutions the band gap is found to increase as shown in the figure 4.4.18. The refractive index and the extinction coefficient of the different films are calculated by the envelope method as suggested by Manifacier \textit{et.al} \({}^{81}\). For the low absorption region of the spectrum the refractive index\((n)\) was calculated using the following expression

\[
 n = \left[ M + \left( M^2 - n_0^2 n_s^2 \right)^{1/2} \right]^{1/2}
\]

(4.7)

Where,

\[
 M = \left( n_0^2 + n_s^2 \right) / 2 + 2n_0n_s(T_{\text{Max}} - T_{\text{Min}})T_{\text{Max}}T_{\text{Min}}
\]

\( T_{\text{Max}}(\lambda) \) and \( T_{\text{Min}}(\lambda) \) are the envelopes connecting the peak(maximum) and the minimum points of the cuve \( T(\lambda) \) respectively. Equation 4.6 can be use to calculate \( n(\lambda) \) and \( k(\lambda) \). The results of the calculation for the different films are shown in figure 4.4.19.a and figure 4.4.19.b. It is noticed that the refractive index decreases with Hf substitution.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure.png}
\caption{Band gaps of the different films calculated from the transmission spectra. The band gap was found to increase for higher Hf concentrations.}
\end{figure}
In summary, the electrical properties of the substituted barium titanate thin films vary depending on the A-site or B-site substitution. Here, only the isovalent substitutions are considered. Tunability and phase transitions can be modified by changing the amounts of substituents. For higher Zr and Hf substitutions the leakage is found to decrease while the tunability decreases. Band gaps are also found to increase with the substitution of more and more hafnium and zirconium.
Chapter 5

Low temperature processing of BST thin films

Any possibility of lowering the crystallization temperature of barium based perovskite is attractive in view of its future applications. Since this thesis involves the processing of barium based perovskites on different types of electrodes, processing for the best properties at lower temperatures would certainly be important. Over the years various methods have been used for low temperature growth of BaTiO$_3$ particles but till date there has been no report of deposition of thin films below 650°C. Even hydrothermal methods used for the synthesis of particles often leave large amounts of hydroxyl ions and are not suitable. Reports of MOCVD based deposition methods for BST thin films show crystallization occurring around 600°C. CSD methods using carboxylate based routes, which are the most commonly used precursors, seldom can be crystallized below 650°C. The main reason for CSD derived films crystallizing above this temperature has often been cited due to the formation of oxo-carbonates. We approach the problem in three different ways. In the first two methods we use normal carboxylate based precursors, which are used extensively, and process them differently in order to see if we can crystallize it at lower temperatures. The third method was developing a new precursor, which would avoid the formation of oxocarbonates.
Low temperature processing of BST thin films

5.1 Changing the oxidizing atmosphere

Since ozone is one of the strongest oxidizing agents, it was used in order to see its effect on crystallization temperature. BST thin films were made by chemical solution deposition of a 0.1 M propionic acid based precursor solution on Pt coated Si substrates. Details of the solution preparation have been provided in chapter 3. In the first set of experiments the solution was deposited on a 4 inch platinized silicon wafer and pyrolysed at 400°C. Coating and pyrolysis was repeated 22 times. This wafer was then diced into 1 square cm pieces. These pieces were then crystallized at various temperatures between 400 and 700°C. It was noticed that the films crystallized only above 650°C. At such temperature even only oxygen leads to some crystallization. Therefore ozone did not help in lowering the crystallization temperature of these thin films.

In another set of experiments, after deposition each layer was crystallized directly at 700°C for 10 min in oxygen. This process was repeated 22 times till the films reached a thickness of approximately 200nm. Top electrodes of Pt were deposited on these films by a photolithographic lift-off process. These films were then post annealed in different ways under oxygen and ozone.

In the following, un-annealed films strictly refer to films without any type of post annealing after top electrode deposition. All the other films after electrode deposition were annealed in oxygen for 5 minutes at 700°C in a rapid thermal annealing (RTA) unit. For the ozone annealed films, after the top electrode was annealed in oxygen in RTA for 5 minutes, it was annealed again in ozone for 30 minutes at different temperatures. This sequence is important because it was noticed that if the films were annealed in the RTA with oxygen after the ozone anneal then the leakage of the films again increased. The RTA step could not be excluded because it ensures a good contact between the top electrode and surface. The ozone annealing was performed at different temperatures (250, 300, 350 and 400°C) to investigate
the effect on the leakage current. An Ozomatic (Modular HC-Series) ozone generator was used for generating the ozone. The ozone concentration was maintained at 4gm/hour for all the ozone annealing processes.

Since all films were derived from 0.1M solutions the microstructure of the films revealed a columnar structure. The ozone annealing has no influence on the microstructure or the crystallization temperature. Films were deposited at low temperature and then ozone annealed at various temperatures between 300°C and 600°C. The films, which were annealed at temperatures below 600°C, show no sign of any crystallization when checked by glancing angle x-ray diffraction (not shown here). For films above 600°C there is usually some degree of crystallization even when annealed in only oxygen. Hence it was impossible to say whether the effect is from ozone or from oxygen. Furthermore at such high temperatures the existence of molecular ozone is questionable.

![Graph](image)

**Fig.5.1.1(a)** Dielectric constant versus frequency of the different films **(b)** Loss tangents versus frequency of the ozone annealed films.

The dielectric constant versus frequency was measured for the different films. It was noticed that after the films were post annealed in oxygen and ozone the dissipation factor decreased. The films, which were unannealed, showed larger dispersion as evident from figures 5.1.1(a) and 5.1.1(b). The dielectric constants versus voltage of the different films are shown in figure 5.1.2. The tunability ($\varepsilon_{\text{max}}-\varepsilon_{\text{min}}$ / $\varepsilon_{\text{max}}$) of the films was found to be
Low temperature processing of BST thin films

approximately between 38 and 42\% for the oxygen and ozone annealed films. The tunability of the films was comparable to bi-layer films deposited by RF sputtering recently reported by

![Graph showing dielectric constant vs voltage for films postannealed in ozone at 350°C, with curves for without top electrode anneal, after TE anneal, and after ozone anneal.](image)

**Fig. 5.1.2** Dielectric constant vs voltage for only the films postannealed in ozone at 350°C is shown in comparison with films without top electrode annealing and films with top electrode annealing in oxygen. Note the slight shift in curve for films without the top electrode anneal.

Liu et.al\[^{84}\] The films, which were not annealed in oxygen or ozone, show a somewhat shifted curve and the reason for such a shift is the difference in the top and bottom electrode interface. The dissipation factor reduces once the films have been annealed in oxygen or ozone. However, there was a slight increase of the dielectric constant with the increase of ozone annealing temperature. Beyond 400°C the ozone annealing did not produce any further increase of the dielectric constant. The increase of the dielectric constant on ozone annealing could be due to the change in the interface capacitance.

The dc leakage currents were evaluated using a step voltage technique. Details have been provided in Chapter 3 of this thesis. Figure 5.1.3 shows the variation in leakage current density with applied electric field for the unannealed, oxygen annealed and ozone annealed BST thin films. It was noticed that the leakage was reduced after a ozone anneal. The reduction in leakage was also dependent on the temperature of the ozone anneal. Films, which were annealed at 350°C in ozone, showed the lowest leakage because of O atoms diffusing
through the film, thereby reducing the number of oxygen vacancies. Any further increase in the ozone annealing temperature did not help in reducing the leakage any further. With increase of temperature the decomposition of ozone into O\textsubscript{2} and O radicals also increases and beyond a certain temperature the collision frequency of the radicals increases and instead of O radicals there is O\textsubscript{2} formation before the wafer is reached. In order to explain the leakage behavior we commence with the standard Schottky mechanism, which is an interface limited transport mechanism.

We commence with the standard reverse biased Schottky equation. This equation is widely applied to the leakage current data analysis for perovskite type titanate thin films\textsuperscript{85,86} and it can be expressed as follows.

\[ J = A T^2 \exp\left(\frac{\alpha E^{1/2} - W_b}{k_B T}\right); \quad \alpha = \left(\frac{q^3}{4\pi \varepsilon \varepsilon_0}\right)^{1/2} \tag{5.1} \]

Agreement with the Schottky barrier model can be verified by plotting the values of Ln \( J \) versus \( E^{1/2} \) for moderately high electric fields\textsuperscript{87,88} From the above equation it
Low temperature processing of BST thin films automatically follows that such a plot should be linear for the Schottky mechanism to be dominant. The value of $\alpha$ was extracted from the slope of this plot and then taken with the slope of the $\text{Ln} \ J/T^2$ versus $1000/T$ plot to determine the barrier height.

![Graph](image1.png)

**Fig. 5.1.4** Ln $J$ vs $E^{1/2}$ plots of the different films. The plots are linear for the ozone annealed films.

![Graph](image2.png)

**Fig. 5.1.5** Ln $J/T^2$ vs $1000/T$ plots of the different films from which the barrier heights were extracted.

Figure 5.1.4 shows the $\text{Ln} \ J$ versus $E^{1/2}$ plots. All the films show a linear region at moderately high fields. This is expected if the leakage current obeys the Schottky mechanism. Figure 5.1.5 shows the plot of the $\text{Ln} \ J/T^2$ versus $1000/T$ plot, which was also linear. The barrier heights for the different films are calculated and shown in the fig. 5.1.6. It was
observed that the barrier heights increase till a post annealing temperature of 350°C in ozone. This may explain

![Graph showing barrier heights versus temperature](image)

**Fig. 5.1.6.** A plot of the different barrier heights versus the ozone post annealing temperature. The barrier height is highest for the films post-annealed in ozone at 350°C.

why there is a reduction of leakage current under conditions that are dominated by the Pt/BST Schottky barrier\(^9^9\). A point defect approach involving reduction of oxygen vacancies has been simulated by Meyer \textit{et al.} for these films and can be found elsewhere\(^9^0\).

Whether the charge transport is interface limited or bulk limited, may also depend on exposing the thin film to moderate or large voltages. Since both mechanisms predict a reduction of the leakage current, further investigation is needed to elucidate the dominating charge transport mechanism.

To summarize, thin films of BST crystallized only around 650°C. Therefore by using a more reactive atmosphere like ozone does not help in lowering the crystallization temperature. However it does help in lowering the leakage current of the films if they are post annealed in the presence of ozone at temperatures between 250 and 400°C. The lowest leakage was observed when the films were post annealed in ozone at 350°C. These results could be explained on the basis of a Schottky barrier increase.
5.2 Laser crystallization of amorphous BST films

This idea of using an excimer laser, to crystallize perovskites, originated from the use of excimer lasers for crystallization of poly-Si based thin film transistors (TFT)\textsuperscript{91,92,93}. Among the techniques that have been proposed to fabricate these poly-Si based TFT’s, excimer laser based crystallization of amorphous Si thin films is the most promising. This is mainly due to the fact that laser crystallization allows for the use of low temperature inexpensive substrates like glass or plastic, since it involves superfast melting and resolidification of the near surface region of the sample and, consequently, minimal heating of the substrate. Furthermore the scanning area can be freely selected without heating other regions. Therefore with this method though the crystallization temperature is not lowered, the disadvantages (destruction of underlying circuits, of high temperature annealing can be avoided. Hence it can be used as a low temperature processing method.

Films were deposited by a carboxylate route. The solutions were deposited on Pt coated Si substrates (Si/SiO$_2$/TiO$_2$/Pt) of 4inch diameter. After deposition of the solution the films were spun at 500rpm for 5 seconds followed by 30 seconds at 4000 rpm. Solutions used were of 0.1 M strength. The coated wafer was pyrolysed each time at 450\degree C. This coating and pyrolysis was performed 11 times to reach the desired thickness of approximately 95 nm. The 4-inch wafers were then diced into $1\text{cm}^2$ pieces. In the first set of experiments these $1\text{cm}^2$ pieces were laser annealed at different fluences and different frequencies while in the second set the films were laser annealed while maintaining a substrate temperature of 250\degree C. Top electrodes of platinum were deposited by a photolithographic lift-off process after an initial SEM examination.

To understand the key parameters during a laser annealing process, thermal simulation is essential. One of the most common equations used to study the problem of heat diffusion on irradiating a complex heterostructure containing the amorphous PZT film is the simplified
one-dimensional heat equation In this model, crystallization and stress development due to inhomogeneous temperature distribution, mismatch of coefficients of thermal expansion between different layers, and material contraction during amorphous to crystalline phase transformation was considered. The governing equations are integrated by finite element method (FEM). A detailed analysis based on FEM was performed by Baldus et.al \textsuperscript{94}. The FEM results shown here are reproduced from the original work to get a basic idea about the fluences appropriate for starting experiments. Without these simulations there would have been an immense number of parameters to change.

On laser irradiation part of the incident radiation is reflected and part of it is absorbed according to the Lambert Law. The absorbed optical energy is converted to thermal energy, including a term that incorporates the heat of fusion (Stefan problem). The following equation describes the non-stationary heat flow.

\[
\frac{\partial (\rho C_p T)}{\partial T} = \nabla (\lambda \nabla T) + q_L
\]  

(5.2)

where \(\lambda\) is thermal conductivity, \(\rho\) is density of the film, \(C_p\) is heat capacity of the material and \(L\) is the heat of fusion. The left side specifies the heat energy accumulated per time interval while the right side gives the difference of the inflowing and outflowing heat. The increasing temperature initiates the transformation from an amorphous to a crystalline phase. Using the Johnson-Mehl-Avrami (JMA) equation (Eq. 5.3), the fraction of the transformed phase \(X\) at time \(t\) is computed.

\[
X(t) = 1 - \exp\left[-(kt)^n\right] \text{with, } k = \exp\left(-E_a / RT\right)
\]  

(5.3)
Low temperature processing of BST thin films

**Fig. 5.2.1** Time dependence of temperature with time at different energy densities for a single KrF pulse.\(^8^7\)

From the simulation it was decided that films around 100 nm would have an interface temperature of about 600ºC which is the minimum temperature required for the crystallization of BST.

**Fig. 5.2.2.**(a) Temperature distribution of the top surface and the bottom interface with time for different film thickness (30, 60, 95, 130, 200nm) (b) Temperature distribution within the heterostructure is shown as a function of depth after 20ns for different laser fluences between 40 mJ/cm\(^2\) and 220 mJ/cm\(^2\) in steps of 20 mJ/cm\(^2\)\(^8^7\).

The heterostructure is shown as a function of depth after 20–ns. It was noticed that there is a large drop in temperature (almost 400ºC) across the TiO\(_2\) layer. In order to reduce the thermal gradient across the TiO\(_2\) layer the second set of experiments was performed while maintaining
a substrate temperature of 250° C. Based on these simulation data the starting laser energy was
decided upon to be 100 mJ/cm² and increased till 150 mJ/cm².

Glancing angle X-ray diffraction was performed on the different films in order to
check the phase formation. Films, which were crystallized with 100, 110, 120 and 150
mJ/cm², are only reported here. Lower energy films were also checked but not shown here
since most of them were non-crystalline. The films, which were irradiated with a higher
energy, were often seen to suffer from larger cracks and ablation. In figure 5.2.3 it is seen that
more number of pulses or a higher energy usually lead to better crystallization. But various
other disadvantages crop up on using higher number of pulses or higher energy, mainly
leading to cracks in the films.

![Graph showing XRD of films crystallized at different fluences and frequencies.](image)

**Fig. 5.2.3.** XRD of the films crystallized at different fluences and frequencies. The X axis shows the 2 theta
values while Y- axis shows the relative intensity. (a) 100 mJ/cm² (b) 110 mJ/cm² (c) 120 mJ/cm² (d) 150
mJ/cm².

cracks. We notice that for frequencies above 80 Hz, there is not much effect in crystallization
(Figure 5.2.3.b). Therefore most of the data are based on films with different energies and
shots but a fixed frequency of 80 Hz.
Low temperature processing of BST thin films

**Fig. 5.2.4.** Films crystallized with different energies (a) 110mJ (b) 120mJ (c) 150mJ (d) 110 mJ while maintaining a substrate temperature of 250°C.

Surface SEM was performed on most of the films deposited in order to study the microstructure development with laser irradiation(Figures 5.2.4 (a), (b), (c) and (d)). Films crystallized with 110 mJ/cm² crystallized with less cracks (figure 5.2.4.a). In figure 5.2.4.b the top surface of the 120 mJ/cm² is shown. When the amorphous film was irradiated with 110 mJ/cm² while maintaining a substrate temperature of 250°C the cracks are minimized further (Figure 5.2.4(d)). Films irradiated with 150 mJ/cm² were found to have large cracks and ablation (figure 5.2.4.c). From the SEM's and, together with numerical simulation studies it was estimated that films treated with 110 mJ/cm² and 120 mJ/cm² while maintaining a substrate temperature of 250°C would be ideal for crystallization.
The leakage of the films was measured and it was found that when irradiated with higher laser energy (120 mJ/cm\(^2\)) the leakage reduced. This is shown in figure 5.2.6. However, beyond

![Fig.5.2.5](image)

**Fig.5.2.5.** Average dielectric constant of the different films at different fluences with 400 shots. Inset shows the dielectric constant versus voltage of the film annealed with 120mJ/cm\(^2\).

The capacitance versus voltage was measured for the films crystallized with different energy densities keeping the frequency (80 Hz) and number of shots (400) fixed (figure 5.2.5). The dielectric constant is found to increase from 60 to 180 for the films when treated by an increasing laser energy, which is quite good considering the thickness of the films to be approximately 95nm. The reason for the low tunability in the films could be due to the different surface layer of the films. Often a low dielectric constant layer at the top electrode interface can lead to low dielectric constant in the total capacitance of the capacitor.

![Fig.5.2.6](image)

**Fig.5.2.6.** Leakage of the films crystallized with different fluences. Films beyond 120 mJ/cm\(^2\) had more microcracks and so were difficult to characterize.

The leakage of the films was measured and it was found that when irradiated with higher laser energy (120 mJ/cm\(^2\)) the leakage reduced. This is shown in figure 5.2.6. However, beyond
Low temperature processing of BST thin films

120 mJ/cm² films were found to suffer from cracks even when the substrates were maintained at 250°C.

5.3 Synthesis of new precursors

In the third method new precursors for the deposition of BST films were developed, since the usual carboxylate based routes lead to formation of intermediate carbonates/oxocarbonates which have been often cited to be the main reason for higher crystallization temperatures. Therefore avoiding them perhaps would lead to lower processing temperatures. Figure 5.3.1. displays the flow chart of the developed CSD process. At first the barium diaminoethoxide \([\text{Ba}(\text{OCH}_2\text{CH}_2\text{NH}_2)_2]\) and strontium diaminoethoxide \([\text{Sr}(\text{OCH}_2\text{CH}_2\text{NH}_2)_2]\) precursors were prepared under dry nitrogen by the dissolution of the pure Ba and Sr metal (Aldrich chemicals, 99.99%) in excess 2-aminoethanol \([\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}]\) at 120 °C.

\[
M + 2 \text{HO-CH}_2\text{CH}_2\text{NH}_2 \xrightarrow{120^\circ\text{C/4h}} M(\text{OCH}_2\text{CH}_2\text{NH}_2)_2 + \text{H}_2 \quad (M = \text{Ba, Sr}) \tag{5.4}
\]

The barium diaminoethoxide and the strontium diaminoethoxide are colourless. A weight percent of the metal diaminoethoxide in 2-aminoethanol is then calculated. Then a calculated amount of these Ba and Sr alkoxides was dissolved into 2-butoxyethanol to prepare a 0.1 M solution. 2-butoxyethanol was used instead of 2-methoxyethanol, which is a commonly used solvent, for chemical solution deposition because of its less toxicity. Subsequently titanium tetra-\(n\)-butoxide \([\text{Ti(O-C}_4\text{H}_9)_4]\) was separately stabilized with two equivalents of acetylacetone \([\text{CH}_3\text{COCH}_2\text{COCH}_3]\) prior to its addition to the alkoxide solution. After mixing, the resulting solution was refluxed for 2 hours at 130 °C. The refluxed solution was cooled and filtered through a 0.2 μm PTFE filter. The entire process has been shown in the
flowchart (Fig. 5.3.1). The solution was then spin coated onto standard Pt coated silicon wafers. After each layer was spin coated the films were crystallized for 20 minutes directly in the diffusion furnace under oxygen atmosphere at various temperatures between 550 °C and 700 °C, since direct high temperature crystallization provided the best results in terms of dielectric properties (section 4.1).

To obtain thicker films the coating procedure was repeated. The thickness per layer of coating was around 8 nm for 0.08M solution, which is comparable to the values obtained for acetate or propionate based BST precursor solutions of the similar concentration (.01 M) reported in chapter 4. In a final step the films were annealed for 1 hour under an oxygen atmosphere. X-ray diffraction patterns were taken to study the crystallization process, orientation and secondary phase formation.

![Flowchart](image)

**Fig 5.3.1** Flowchart describing the preparation of BST thin films by the aminoethoxide route.
Low temperature processing of BST thin films

Figures 5.3.2 show the relative TGA and the DTA curves of the Sr and Ba diaminoethoxides and the BST solution from which the complete decomposition behaviour can be studied. The thermogravimetric analysis shows a constant loss up to 500 °C. It can be seen that most of the weight loss occurs below 200 °C. This could be attributed to the evaporation of the free 2-aminoethanol (b.p. 170 °C) which is corresponding to a small endothermic peak on the DSC curve. The weight loss between the temperature range of 200 and 500 °C is considered to result from the decomposition of the 2-aminoethoxy ligands.

Fig. 5.3.3. (a) XRD of films derived from aminoethoxide route (b) XRD of films derived from normal carboxylate group

bonded to the metal atoms. Figures 5.3.3 shows glancing angle X-ray diffraction at different deposition temperatures between 550 °C and 700 °C. The BST films were found to crystallize...
only above 600 °C. Some authors have previously reported that this high temperature of crystallization, which is typically found for alkaline earth titanate thin films, is due to the formation of an intermediate oxo-carbonate phase (e. g. Ba$_2$Ti$_2$O$_5$CO$_3$)\textsuperscript{96,97}. This oxo-carbonate phase formed in most cases when a carboxylate based precursor solution was used. This was most likely due to already present “carbonate like linkages” within the metal carboxylates which during pyrolysis form the thermodynamically stable oxo-carbonates. In thin films this carbon rich phase is stable up to 650 °C\textsuperscript{98}. Recent studies by Lotnyk\textit{et.al.}\textsuperscript{99} between evaporated BaCO$_3$ and rutile TiO$_2$ single crystals show the existence of the BT phase only above 600 °C. The amount of BT formed at 600°C is quite low and cannot be detected by normal X-ray diffraction methods. Only pole figures of the samples were able to detect the small amounts of the BT phase at 600°C. Also the authors have shown that energetically it is more favourable for the BaCO$_3$ phase to react with the TiO$_2$ rather than the BaCO$_3$ to dissociate first and then react with TiO$_2$. When carboxylate based precursors are used they decompose into carbonates/oxocarbonates and TiO$_2$. Thus the reacting components are similar here as compared to those of Lotnyk. However there is one difference, since Lotnyk evaporated the BaCO$_3$ onto the surface of TiO$_2$, the diffusion distance of the BaCO$_3$ is slightly larger than in this case where the TiO$_2$ grains are within the matrix of barium carbonate/oxocarbonate\textsuperscript{93}. Perhaps this is the reason for the high (900°C) temperatures required for complete conversion to BT.

Hence in this study we have used non-carboxylate based precursors which do not have this ‘carbonate like linkages’ and therefore the formation of the intermediate oxo-carbonate/carbonate phase can be avoided as can be seen from the FT-IR graphs (Fig. 5.3.4). The FT-IR was performed on the BST samples deposited on Pt coated Si substrates. The presence of any carbon rich phase would have been indicated with a band between 1400 cm$^{-1}$ and 1600 cm$^{-1}$. 

Low temperature processing of BST thin films

Hasenkox et al. have done a detailed temperature dependent FT-IR study on the carboxylate routes and found that single phase barium strontium titanium titanate formed only around 650 °C. The absence of carbon rich phase was noticed even at temperatures as low as 500 °C. However the onset of crystallization did not occur below 600 °C. Liedtke et al. had amorphised crystalline BST films by oxygen ion implantation and then tried to re-crystallize it. It was observed that the films did not show any significant perovskite phase formation below 600 °C. Crystallization temperatures required in MOCVD methods for depositing BST are also around 600°C\(^{100}\). These findings indicate that the formation of oxo-carbonate phases is not the only reason for the typically observed high crystallization temperature of BST thin films.

The microstructure of the film plays an important role in achieving a high dielectric constant of the film. It is a known fact that columnar microstructure yields films of higher dielectric constant. It had been reported by Schwartz\(^{101}\) that PZT favours heterogeneous nucleation and hence it forms usually columnar microstructure but for BST it is slightly more tricky since BST favours homogeneous nucleation. Gust et al.\(^{102}\) had performed TEM studies and had shown that during the initial stages of crystallization nano TiO\(_2\) grains act as seeds for
the crystallization. Therefore homogeneous crystallization is favoured. Hoffmann *et al.*\textsuperscript{103} had shown that by decreasing the concentration of the carboxylate based solution reduces the thickness of each layer deposited. This almost forces the amorphous layer to nucleate heterogeneously and therefore leads to films with columnar structure. Hence the evolution of microstructure with ongoing film crystallization was studied with SEM. The films were deposited with a 0.1 M solution. Figure 5.3.5(a) is the cross-sectional view of the amorphous film with hardly any distinguishable grains. With increasing processing temperature the grains grow larger and become more dense as can be seen from the figures 5.3.5(b), 5.3.5(c), and

![Fig 5.3.5(a)](image1)

![Fig 5.3.5(b)](image2)

![Fig 5.3.5(c)](image3)

![Fig 5.3.5(d)](image4)
Low temperature processing of BST thin films

Fig. 5.3.5. SEM pictures of the films deposited by the aminoethoxide route at (a) 550°C with 0.1 M concentration (b) 600°C with 0.1M (c) 650°C with 0.1M (d) 700°C with 0.1M (e) 700°C with 0.08M (f) 700°C with 0.1M carboxylate route.

5.3.5(d). In agreement with the previously mentioned conditions for heterogeneous nucleation of BST thin films, an almost perfectly columnar structure (Fig. 5.3.5e) of the films was only obtained when very dilute solutions (0.08 M) were used. For comparison columnar structured films derived from the usual carboxylate precursors are shown in fig 5.3.5.f. These columnar films showed a much higher dielectric constant. Experiments with higher concentrated precursor solutions (e.g. 0.3 M, not shown here) only yielded coarse grained microstructures.

Fig. 5.3.6. Variation of dielectric constant with temperature for the aminoethoxide derived films at 700°C.

After synthesis and processing of the BST films, 100 nm thick top electrodes were sputter deposited and patterned by a lift off process. The area of the electrodes was 0.125
mm$^2$. The thickness of the films was determined with a profilometer DEKTAK$^3$ST (Veeco Instruments Inc.) after etching away a part of the film. All films were 200 nm thick. Fig. 5.3.6 shows the plot of dielectric constant versus temperature. The average dielectric constant versus voltage is shown in Fig. 5.3.7 at three different frequencies. A small alternating current signal of 50 mV amplitude was applied while the dc electric field was swept from positive bias to negative bias$^{104}$. The tunability of the films was found to be around 37% at 100 kHz. The dielectric constant of the films was found to increase with increase of deposition.

![Graph](image1)

**Fig. 5.3.7(a)** Permittivity versus voltage of the aminoethoxide derived films at 700°C with 0.08M solution. **(b)** permittivity versus voltage of the carboxylate route derived films 700°C with 0.1M solution.

![Graph](image2)

![Graph](image3)

**Fig. 5.3.8.** (a) Increase of dielectric constant with temperature for the aminoethoxide films with 0.1M solution and columnar films with 0.08M solution at 700°C. **(b)** increase of dielectric constant with temperature for the carboxylate derived columnar films.
Low temperature processing of BST thin films

temperature. However beyond 700 °C it was almost constant. This is shown in Fig. 5.3.8. The dielectric constant of the films were quite high (440) for the 200 nm thick films and similar to carboxylate route based films which show a dielectric constant around 400 for 190 nm thick film.

The current voltage characteristics ($I-V$) were measured as functions of temperature and applied voltage. The details have been described in the electrical characterization section of chapter 3. The basic conduction mechanisms in insulating films can be classified into electrode-limited or bulk limited conduction\textsuperscript{105}. In Pt/BST/Pt capacitors the main current conduction mechanisms are electrode limited, i.e. either Schottky emission or Fowler-Nordheim tunnelling, or a combination of both\textsuperscript{106-108}. To determine whether the operating mechanism controlling the leakage is really Schottky it is essential to investigate both the field dependence and the temperature dependence of the leakage current. In fig. 5.3.9 the leakage current characteristic for different temperatures is presented in a log ($J$) vs $E$ plot. The leakage of these films prepared by the aminoethoxide route is found to be comparable to those prepared by the carboxylate route.

To summarize, barium and strontium 2-aminoethoxides were successfully used as precursors in a new CSD route for the fabrication of high quality BST thin films, which

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig5_3_9.png}
\caption{Comparison of leakage of the aminoethoxide and carboxylate derived films. Open circles for carboxylate derived films and filled symbols for aminoethoxide derived films.}
\end{figure}
enables the complete decomposition of the organics below 500 °C and completely avoids the formation of an intermediate oxo-carbonate phase during crystallization. Obviously the change of the precursor chemistry leads to a modified decomposition and crystallization pathway. The 2-aminoethoxides based solutions were less sensitive to moisture as compared to other metal alkoxides and therefore the shelf life of the precursor solutions is longer than those of the typical carboxylate based precursor solutions. The dielectric constant of the 200 nm thick films prepared by this route were around 440 and were comparable to the dielectric constant (400) of films produced by carboxylate routes. The tunability of the films was around 37% at 100 kHz. The dielectric constant of the films increased with the increase of annealing temperature but beyond 700 °C it did not show any significant increase. The leakage conduction mechanisms of the deposited films were studied and they were found to be comparable to those prepared by the carboxylate route. All films crystallized only above 600 °C even though the oxo-carbonate phase was avoided during the crystallization of the BST films. This is still a lower deposition temperature as compared to films deposited by the carboxylate route. From the presented results it is concluded that the formation of oxo-carbonate phases is not the only reason for the high crystallization temperatures in CSD processing of BST thin films. Probably the “structure” of the amorphous phase, which forms after the decomposition of the organics before the final crystallization, plays another important role.
Chapter 6

Integration of CSD derived ceramic films with base metal electrodes

Manufacturers of multilayered ceramic capacitors based on BaTiO$_3$ based systems until recently used palladium or silver palladium based alloys for the inner electrode. For cost reduction, these expensive noble metals and their alloys are being replaced by cheaper base metal electrodes like nickel/copper. Since these base metal based internal electrodes would be easily oxidized during ambient firing. Firing has to be carried out in a reducing ambient. Usually firing of multilayer ceramic capacitors is done in a variety of reducing atmospheres like N$_2$/H$_2$ or N$_2$/H$_2$/H$_2$O and CO/CO$_2$. In such reducing conditions and high temperatures a large number of oxygen vacancies is formed giving rise to poor insulation resistances. The study of nonreducible dielectrics for producing Ni-MLCC’S was started by Herbert in the early 1960’s$^{109}$. Upto 1970’s the development of nonreducible dielectrics was mainly achieved by the addition of acceptors like Fe$^{3+}$/Mn$^{2+}$/Cr$^{3+}$.$^{110,111,112}$ The conduction electrons can be effectively trapped by incorporation of acceptor ions (Fe$^{3+}$,Mn$^{2+}$,Cr$^{3+}$) in the B-site perovskite lattice. However, capacitors with base metal electrodes containing acceptor doped BaTiO$_3$ dielectrics did not show satisfactory values of insulating resistance especially under
time dependent electrical stress due to the ionic conductivity caused by the mobility of the charged oxygen vacancies in the electric field. To enhance the reliability of BaTiO$_3$ dielectrics one may incorporate acceptor donor mixtures like Mn-Nb or Mn-W, in combination with re-oxidation treatment. More recently studies on ‘magic’ dopants have been found to be very effective in improving the reliability of BaTiO$_3$ capacitors. They are Y$^{3+}$, Dy$^{3+}$ and Ho$^{3+}$.$^{113,114}$ These have amphoteric character and are able to occupy both A or B sites. Depending on the amount of dopants, the relative ratio B/A varies and therefore either the donor or acceptor character prevails.

With trends towards thinner dielectric layer thickness and larger capacitance of Ni-MLCC, new deposition methods are being sought which would be cheap and simple as the tape casting methods used now. One of the alternatives for the method of fabrication of ceramic thin films in a cheap and effective way is the use of chemical solution deposition methods. CSD methods have been used for the fabrication of thin films between 40-1000nm for different purposes like coated conductors, ferroelectric devices, MEMs applications and tunable devices but until now it had has not been used much in the MLCC industry because conventional tape casting methods were able to satisfy the required dielectric thickness needs. But, in the near future it is envisaged that dielectric thicknesses in the mesoscopic thickness range of 300-800 nm would be required to meet the very high capacitance densities. Since CSD methods can be used easily for the deposition of dielectrics in this thickness range it is being considered as the most probable method of deposition. Moreover, the complex composition of the non-reducible dielectric compositions can be easily achieved in solution form while maintaining accurate stoichiometry. Some commonly cited disadvantages, like a large number of coating steps, have been already taken care of by various groups by changing the precursor chemistry. The use of microemulsions or colloidal dispersions in conjunction with MOD solutions (chapter 6 in this work) can be used to take care of such disadvantages.
Integration of CSD derived films with base metal electrodes

Previous work in the MLCC industry mostly dealt with the fabrication of ceramic powders and their application on Ni foils/electrode pastes. MLCC’s are usually fabricated in the following way. An electrode paste of fine internal electrode paste is applied by screen printing onto a dielectric green sheet. A pre determined number of sheets are stacked, pressed and cut into pieces. After burning out the binder, the chips are fired. In order to sinter both the ceramic and the electrode, it is important to control the shrinkage behavior of each material and the firing conditions. In this method the ceramic dielectric powders and electrode powders were synthesized separately and then applied as a paste for the formation of a green body at high temperatures. In order to use a CSD based method the fabrication way is different. The solution is deposited onto the foil first, dried and then pyrolysed. This process of drying and pyrolysis is usually repeated before crystallization in order to reach a mesoscopic thickness range. If each layer is deposited and crystallized then it would increase the number of heating steps. Therefore it is required to optimize the number of layers to be deposited, dried and pyrolysed before a crystallization can be performed. Lower the thickness of the dielectric layer larger the capacitance density, but at this stage it should be remembered that if the dielectric layer thickness is too low during multiple layer processing two corresponding layers might get short circuited leading to a failure of the device. Thus optimization of layer thickness with electrodes is of utmost importance.

6.1 CSD of BT based compositions on Ni foils

Nickel foils were obtained from Alfa Aesar (99.99%) purity. These foils were polished at first by chemical mechanical polishing (CMP). Without polishing the foils, the foil surface was found to be too rough. Once the nickel foils were polished they were cleaned with acetone and isopropanol for 10 minutes each in the ultrasonic cleaner. These films were then cleaned and used as substrate for deposition of the CSD solution. A schematic of the
deposition process is shown in the figure 6.1.1. The films are pyrolysed for 5 minutes at 350°C in air. This process is repeated 4 times before placing them at the edge of the tube.

![Fig. 6.1.1. Schematic for the preparation of ceramic thin films by CSD on Ni foils](image)

The films are then placed in the quartz glass tube of the furnace, and it is flushed with the N₂/H₂ (1% forming gas) for 3 minutes before moving the tube inside the tube furnace. This flushing step is important because if the nickel foil coated with the film is directly placed in the hot zone, the resident oxygen is enough to oxidize the nickel electrode at such a high temperature. Each crystallization process lasted for 30 minutes. For the nickel foils the atmosphere was always 1% forming gas. The details of the experimental setup have been provided in chapter 3. Three different material systems were investigated; BaTiO₃, (Ba,Sr)TiO₃ and Ba(Ti,Zr)O₃. Each one of these compositions was processed at 3 different temperatures at 800°C, 900°C and 1000°C while maintaining the forming gas concentration at 1%. Top electrodes of Ni(30 nm) + Au(100nm) were thermally evaporated onto them. This specific configuration was chosen simply in order to maintain a symmetric electrode structure with the ceramic dielectric in between. Top electrodes of only Ni were not possible because the tungsten boats containing
Integration of CSD derived films with base metal electrodes

the nickel for evaporation often got destroyed after 10nm of deposition due to the formation of an alloy.

The BaTiO$_3$ solution was prepared by the standard propionate route as described in chapter 3 of this thesis. The solution was spin coated on Ni foils at 500 rpm for 5 seconds and then at 3000 rpm for 30 seconds. The procedure is depicted in figure 6.1.1. X-ray diffraction pattern of the films crystallized at 3 different temperatures are shown in figure 6.1.2. With increase in temperature the crystallinity increases and this is evident from the sharper

![Graph showing X-Ray diffraction of the BaTiO$_3$ films crystallized at three different temperatures of 800$^\circ$C, 900$^\circ$C and 1000$^\circ$C. Clearly the intensity of the peaks increases with increase in temperature.]

**Fig.6.1.2.** X-Ray diffraction of the BaTiO$_3$ films crystallized at three different temperatures of 800$^\circ$C, 900$^\circ$C and 1000$^\circ$C. Clearly the intensity of the peaks increases with increase in temperature.

![Surface SEM micrographs of BaTiO$_3$ (a) Film crystallized at 800$^\circ$C, (b) Film crystallized at 900$^\circ$C (c) Film crystallized at 1000$^\circ$C.]

**Fig. 6.1.3** Surface SEM micrographs of BaTiO$_3$ (a) Film crystallized at 800$^\circ$C, (b) Film crystallized at 900$^\circ$C (c) Film crystallized at 1000$^\circ$C.

reflections. The surface SEM scans show an increased grain size with temperature (figure 6.1.3). Average grain size increased from about 40 nm to 80 nm. Also, evident from the SEM
micrographs is the reduction of the number of pores with higher temperatures. The dielectric constant of the BT thin films was found to increase with increase of crystallization temperature due to the increase in grain size (fig.6.1.4.a). Tunability of the films crystallized above 900°C is significantly higher than films annealed at 800°C (Fig. 6.1.4.a). Re-oxidation of the films in dry N₂ increases the values of the dielectric constant significantly (Fig.6.1.5).

Thin films of (Ba₀.₇Sr₀.₃)TiO₃ were also prepared from the standard propionate precursor based solution. They were also deposited in the same way as the BT thin films.
Integration of CSD derived films with base metal electrodes described previously. In a similar fashion higher temperatures lead to an increased crystallinity and this is reflected in the XRD graph (Fig. 6.1.7) shown below.

![XRD graph](image)

**Fig. 6.1.6.** X-Ray diffraction patterns in the 0-2θ mode of the (Ba$_{0.7}$Sr$_{0.3}$)TiO$_3$ films crystallized at three different temperatures of 800°C, 900°C and 1000°C. Intensity of the peaks increases with increase in temperature. For comparison an XRD of the pure Ni foil is included.

For the (Ba$_{0.7}$Sr$_{0.3}$)TiO$_3$ as compared to the BT thin films, the SEM pictures show an enhanced grain growth with temperature (fig.6.1.7). If we compare the grain size of BST thin films at 1000°C with the grain size of BT films at 1000°C we notice that the grain size is larger in this case which is due to the substitution of the larger Ba ions with the smaller Sr ions. The smaller Sr ions can diffuse faster and therefore this leads to larger grains. From graph 6.1.8.a

**Fig.6.1.7 Surface SEM micrographs of (Ba$_{0.7}$Sr$_{0.3}$)TiO$_3$ (a) Film crystallized at 800°C, (b) Film crystallized at 900°C (c) Film crystallized at 1000°C.
we can see that the dielectric constant increases with increase of annealing temperature, while the dielectric loss is found to decrease. As for the BT thin films, here too the tunability of the

![Graph](image1.png)

**Fig. 6.1.8.(a)** C-F measurements for (Ba$_{0.7}$Sr$_{0.3}$)TiO$_3$ films crystallized at different temperatures and (b) tunability of the film as a function of temperature.

BST films increases greatly for films crystallized above 900°C (Fig. 6.1.8.a).

In another set of experiments Ba(Ti$_{0.9}$Zr$_{0.1}$)O$_3$ films were also deposited from the standard propionate precursors on nickel foils at three different temperatures. X-ray diffraction patterns show them to be pure perovskite in nature without any trace for secondary

![Graph](image2.png)

**Fig. 6.1.9.** X-Ray diffraction in the 0-2θ mode of the Ba(Ti$_{0.9}$Zr$_{0.1}$)O$_3$ films crystallized at three different temperatures of 800°C, 900°C and 1000°C. Clearly the intensity of the peaks increases with increase in temperature. For comparison an XRD of the pure Ni foil is included.
Integration of CSD derived films with base metal electrodes

phase. Again increased crystallization temperatures led to larger grains and more intense reflection peaks in the XRD (fig. 6.1.9). Surface SEM’s (figure 6.1.10) show an increase in grain size with temperature as was noticed for the others.

![Surface SEM micrographs of Ba(Ti$_{0.9}$Zr$_{0.1}$)O$_3$](image)

**Fig. 6.1.10** Surface SEM micrographs of Ba(Ti$_{0.9}$Zr$_{0.1}$)O$_3$ (a) Film crystallized at 800°C, (b) Film crystallized at 900°C (c) Film crystallized at 1000°C.

![Graphs showing dielectric constant and dissipation factor](image)

**Fig. 6.1.11.(a)** C-F measurements for Ba(Ti$_{0.9}$Zr$_{0.1}$)O$_3$ films crystallized at different temperatures and (b) tunability of the different films.

The frequency domain response of the dielectric constant shows an increase in dielectric constant with higher crystallization temperatures (fig.6.1.11.a). Tunability of the films is also found to increase with increase in crystallization temperature but compared to BT and BST tunability of around 60% is achieved only after the films are annealed at 1000°C (fig. 6.1.11.b). In general all barium-based perovskites show an increase in the dielectric constant with increase of annealing temperature.
In all these films, which have been processed at temperatures above 800°C the dielectric constant values achieved, is much higher than in normal platinized silicon wafers, which were processed at 700°C (Chapter 4). In order to see the effect of such high temperature of crystallization of BT, BST and BTZ films specially prepared platinized wafers were used. These wafers had AlO\textsubscript{x} as an adhesive layer for the Pt (Chapter 3). Since these wafers were optimized for 900°C. The graphs (Fig.6.1.12) show the dielectric constant values of BT/BST/BTZ films crystallized at 700°C in normal (Si/SiO\textsubscript{2}TiO\textsubscript{2}/Pt) wafers and at 900°C with Si/SiO\textsubscript{2}AlO\textsubscript{x}/Pt wafers.

![Graphs showing dielectric constant versus voltage of BT and BST films crystallized at 700°C and 900°C.](image)

**Fig. 6.1.12.(a)** Dielectric constant versus voltage of BT thin films crystallized at 700 and 900°C. (b) Dielectric constant versus voltage of BST thin films crystallized at 700 and 900°C. All measurements at 10kHz.

![Surface SEM scans](image)

**Fig. 6.1.13.(a)** BT deposited at 700°C (b) BT deposited at 900°C (c) BST deposited at 700°C (d) BST deposited at 900°C.

Surface SEM scans show that indeed with increase of crystallization temperature the grain size increases (fig 6.1.13). The reason for the higher dielectric constant could be the enhanced grain growth at higher temperatures. Therefore the higher dielectric constants achieved when
Integration of CSD derived films with base metal electrodes

processing on foils is mainly due to the effect of grain growth. Depending on the application and thermal budget of processing dielectric properties will differ.
Chapter 7

Microemulsion based CSD (µE-CSD)

The term ‘microemulsion’ was first used by Schulman\textsuperscript{115} in 1959 for colloidal systems which are thermodynamically stable, optically isotropic dispersions of two-non miscible liquids stabilized by amphiphilic compounds. These systems have domains of 100 nm or less dispersed in a continuous phase. Thus, in fact they are ‘nanoemulsions’ regarding the dimensions of their internal structures. Microemulsions can be used for the synthesis of a variety of nanoparticles\textsuperscript{116,117}.

Microemulsions in contrast to macroemulsions are isotropic, optically transparent and thermodynamically stable dispersions of oil in water or water in oil. They have been investigated with small angle x-ray scattering\textsuperscript{118}, dynamic light scattering\textsuperscript{119} and electron microscopy\textsuperscript{120}. These studies show that in the relevant regions of the ternary or quaternary phase diagrams, the dispersed phase exists as uniform droplets with size ranging from 5-100nm. All types of surfactants (nonionic, anionic, cationic and zwitterionic) and a large variety of co-surfactants can be used for the stabilization of the micelles. The co-surfactants shape the tertiary structure of the surfactants and thus shapes the supramolecular structure. These supramolecular units of surfactant and co-surfactant molecules continuously exchange surfactant and other molecules with the surroundings\textsuperscript{121}. And, because of this, these micellar
Microemulsion based CSD structures can be used as nanoreactors i.e. a confined nanoscale space for a large variety of chemical reactions. By proper choice of the surfactant/co-surfactant the size and shape of the ‘nanoreactors’ can be adjusted.

In the presence of surface-active reagents, the interfacial tension of a water-oil-interface decreases, appreciably, in particular if a co-surfactant is added due to the penetration of the surfactant molecule into the surfactant film at the interface. This has been schematically shown in the figure 7.1. If the amount of surfactant and co-surfactant at the interface is large enough, the spreading pressure maybe sufficiently high to produce very small or negative values of the interfacial tension. Development of this low interfacial tension leads to the spontaneous formation of a microemulsion. The tendency to form a large number and small sized droplets is limited by the maximum interface area between water and oil which can be stabilized by the surfactant/cosurfactant film. As an example we show the formation of a microemulsion formed between cyclohexane and water with the help of surfactant/co-surfactant.

Figure 7.1 A micelle depicting water in oil structure.
The water in the microemulsion can be used as a reactant for the synthesis of nanoparticles. Nanocrystalline BaTiO$_3$ can be synthesized by using microemulsion mediated synthesis. The approach used relies on the hydrolytic decomposition of a mixed Ba-Ti-isopropoxide solution in a microemulsion composed of 10.47% Tergitol NP 35 as surfactant, 87.70 wt% cyclohexane as hydrophobic phase, 3.79 wt% of ultra pure degassed water. After the preparation of the metallo-organic precursor solution, a stoichiometric amount of the microemulsion is added dropwise at room temperature$^{123}$. This leads to the formation of water free organosols and BaTiO$_3$ particles coated with a surfactant shell are formed (Fig. 7.2). This water –free clear colloidal solution of nanocrystalline BaTiO$_3$ can be used for a variety of purposes from synthesis of special ceramics to thin films of mesoscopic thickness.

$$[\text{BaTi(O-R)}_n]_m + \text{H}_2\text{O} \rightarrow \text{BT}$$

**Figure 7.2** A representation of the reaction mechanism. The precursor is added to the microemulsion for the generation of the BT dispersion.

The trend towards miniaturization of electric modules containing multilayered ceramic capacitors (MLCCs), micro electromechanical systems (MEMs) and low temperature co-fired ceramic capacitors (LTCCs) requires a continuous reduction of layer thickness and finer ceramic powders. For most applications that require a high dielectric constant BaTiO$_3$ based ceramic layers are normally used. The traditional technology used for the fabrication of multilayer’s involving BaTiO$_3$ based dielectrics is tape casting. At present, the thinnest layers that can be achieved using this process are around 1 µm. The main problem is in the fabrication of smaller particles which can be used for the fabrication of the green paste$^{124}$.  

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Microemulsion based CSD

Tape casting has been favored over other methods mainly due to cost reasons and also due to its ease of manufacturability. In such a scenario, only chemical solution deposition methods are an alternative for such a mass scale production, but it too has certain limitations. Application of standard CSD based methods for mesoscopic thicknesses between 500 – 800 nm can be cumbersome due to the number of coatings. This problem can be solved by the use of stable colloidal dispersions containing a substantially high amount of solid nanoparticles. Since these colloidal solutions are alcohol based they can be spin coated onto different substrates. One general problem faced when these colloidal solutions are used for spin coating films is the formation of pores. If these pores are not filled, the lifespan of the capacitors is reduced. In order to reduce porosity and increase the reliability of the dielectric layer, these colloidal solutions containing 5 wt% BT were used with various volume percents of normal BT CSD solutions of concentration 0.1693M. The following table shows the various volume percents of colloidal solutions and CSD solution mixed for the different films. It is noticed that with increase of volume percent of the CSD solution the thickness achieved per layer decreases (Table 7.1), which is expected since the amount of the colloidal particles

<table>
<thead>
<tr>
<th>Volume of colloidal solution 5 wt% BT</th>
<th>Volume of CSD solution (0.1963 M)</th>
<th>Method of heating, 700°C</th>
<th>Thickness Dielectric Constant (10kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 %</td>
<td>0%</td>
<td>Diffusion Oven</td>
<td>660 nm (5C) 132 nm/layer 400</td>
</tr>
<tr>
<td>90 %</td>
<td>10%</td>
<td>Diffusion Oven</td>
<td>500 nm(5C) 100 nm/layer 395</td>
</tr>
<tr>
<td>80%</td>
<td>20%</td>
<td>Diffusion Oven</td>
<td>570 nm(6C) 95 nm/layer 500</td>
</tr>
<tr>
<td>70%</td>
<td>30%</td>
<td>Diffusion Oven</td>
<td>390 nm(5C) 78 nm/layer 425</td>
</tr>
<tr>
<td>60%</td>
<td>40%</td>
<td>Diffusion Oven</td>
<td>260 nm(5C) 52 nm/layer 300</td>
</tr>
</tbody>
</table>

Table 7.1. The table above gives the different ratios of the microemulsion mixed with CSD solution. Thickness per layer is found to decrease with increase in volume content of the CSD solution. Dielectric constant was found to vary between 300 and 500. Note that both the colloidal solution and CSD solution are of equal molarity.
decreases. The dielectric constant achieved for the films varies between 300 and 500. A variety of factors can be influencing these phenomena, like thickness (larger grains possess higher dielectric constant), pores and substrate effect in conjunction with thickness. Furthermore the colloidal particles, which were synthesized and found to be approximately 10 nm, have certainly increased in size. This could have happened during crystallization or the micelles themselves could have been affected during the mixing with the MOD solution. The dielectric constant versus voltage of each type of film is displayed alongside the SEM micrograph. The dielectric constant change with different MOD contents can be explained by a combination of change in grain size, change in porosity and also thickness of the films.

![Cross-sectional SEM of films derived from the nano BT dispersions.](image1)

![Permittivity versus voltage of the films at 10kHz](image2)

**Fig. 7.3.(a)** Cross-sectional SEM of films derived from the nano BT dispersions. **(b)** Permittivity versus voltage of the films at 10kHz

![Cross-sectional SEM of films derived from the nano BT dispersions mixed with 10 volume percent MOD solution derived by the normal standard propionate route.](image3)

![Permittivity versus voltage of the films at 10kHz](image4)

**Fig. 7.4.(a)** Cross-sectional SEM of films derived from the nano BT dispersions mixed with 10 volume percent MOD solution derived by the normal standard propionate route. **(b)** Permittivity versus voltage of the films at 10kHz.
Microemulsion based CSD

Fig. 7.5.(a) Cross-sectional SEM of films derived from the nano BT dispersions mixed with 20 volume percent MOD solution derived by the standard propionate route. (b) Permittivity versus voltage of the films at 10kHz.

Fig. 7.6.(a) Cross-sectional SEM of films derived from the nano BT dispersions mixed with 30 volume percent MOD solution derived by the standard propionate route. (b) Permittivity versus voltage of the films at 10kHz.

Fig. 7.7.(a) Cross-sectional SEM of films derived from the nano BT dispersions mixed with 40 volume percent MOD solution derived by the standard propionate route. (b) Permittivity versus voltage of the films at 10kHz.
also thickness of the films. All the above films were deposited on platinized substrates and then placed in the diffusion oven which is similar to the processing of BT based films by conventional CSD. The second set of films was processed in the RTA. Films were derived from the same solution composition as above, but this time after deposition they were directly crystallized in the rapid thermal annealing system with the following temperature profile.

![Heating ramp of the RTA used for the crystallization of the films derived from the hybrid solution of the BaTiO$_3$ colloidal dispersions with BaTiO$_3$ MOD solution.](image)

**Fig. 7.8.** Heating ramp of the RTA used for the crystallization of the films derived from the hybrid solution of the BaTiO$_3$ colloidal dispersions with BaTiO$_3$ MOD solution.

<table>
<thead>
<tr>
<th>Volume of colloidal solution (5 wt% BT)</th>
<th>Volume of CSD solution (0.1693 M)</th>
<th>Method of heating. 700°C</th>
<th>Thickness</th>
<th>Dielectric Constant (10kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100%</td>
<td>0%</td>
<td>RTA</td>
<td>580nm (5C) 116 nm/layer</td>
<td>380</td>
</tr>
<tr>
<td>90%</td>
<td>10%</td>
<td>RTA</td>
<td>460 nm(5C) 92 nm/layer</td>
<td>710</td>
</tr>
<tr>
<td>80%</td>
<td>20%</td>
<td>RTA</td>
<td>390 nm(5C) 78 nm/layer</td>
<td>920</td>
</tr>
<tr>
<td>70%</td>
<td>30%</td>
<td>RTA</td>
<td>290 nm(5C) 58 nm/layer</td>
<td>1100</td>
</tr>
<tr>
<td>60%</td>
<td>40%</td>
<td>RTA</td>
<td>200 nm(5C) 40 nm/layer</td>
<td>1050</td>
</tr>
</tbody>
</table>

**Table 7.2.** The table above gives the different ratios of the microemulsion mixed with CSD solution. Thickness per layer is found to decrease with increase in volume content of the CSD solution. While dielectric constant was found to increase considerably with increase of MOD solution content.

It is noticed that there is a large difference in the grain structure for the films derived from the hybrid solution (consisting of the colloidal dispersion and the BT MOD solution), and crystallized in the RTA, as compared to the diffusion oven processed films (Figures 7.3-7.7).
Microemulsion based CSD

When crystallized in the RTA the grains tend to grow much larger and have higher dielectric constants. Figure 7.9.a shows the cross sectional SEM of a film derived from only a BT dispersion. The dielectric properties are shown in the figure alongside the SEM (Fig. 7.9.b). Here the dielectric constant values are comparable to those of the diffusion oven processed films. In figure 7.10.a we can see that with addition of the BT MOD solution (10% ) the

Fig. 7.9.(a) Cross-sectional SEM of films derived from the nano BT dispersions crystallized in the RTA. (b) Tunability and variation of the dielectric constant with temperature. Inset shows the dielectric constant versus voltage of the films.

Fig. 7.10.(a) Cross-sectional SEM of films derived from the nano BT dispersions and 10 volume percent BT MOD solution crystallized in the RTA. (b) Tunability and variation of the dielectric constant with temperature. Inset shows the dielectric constant versus voltage of the films.
Grains have become bigger, thereby showing a large increase in the dielectric constant (Fig. 7.10.b). With 20% BT MOD solution mixed, the films become denser and the dielectric constant increases to 910 (Fig. 7.11). Further increase in the volume percent of the MOD solution (30%), leads to a almost columnar grain growth (Fig. 7.12.a), while for 40% it is perfectly columnar. The dielectric constant is around 1100 for both films derived from 30% and 40% hybrid solutions. At this point it is instructive to note that columnar films have been reported previously, grown by using only CSD of similar thicknesses, however in order to grow a film of around 400nm thickness typically 45 or more coatings was required.\textsuperscript{62}

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**Fig. 7.11.** (a) Cross-sectional SEM of films derived from the nano BT dispersions and 20 volume percent BT MOD solution crystallized in the RTA. (b) Tunability and variation of the dielectric constant with temperature. Inset shows the dielectric constant versus voltage of the films.

**Fig. 7.12.** (a) Cross-sectional SEM of films derived from the nano BT dispersions and 30 volume percent BT MOD solution crystallized in the RTA. (b) Tunability and variation of the dielectric constant with temperature. Inset shows the dielectric constant versus voltage of the films.
The dielectric constant achieved for the changes in the grain structure of the films when crystallized in the diffusion oven and RTA can be explained on the basis of a hypothetical model based on the standard nucleation theory. Equations 7.1 and 7.2 describe the free energy barriers homogeneous and heterogeneous nucleation respectively.

\[
\Delta G_{\text{homo}} = \frac{16\pi\gamma^3}{3(\Delta G_v)^2}
\]

\[
\Delta G_{\text{hetero}} = \frac{16\pi\gamma^3}{3(\Delta G_v)^2} \cdot f(\theta)
\]

where \(\gamma\) is the interfacial energy and \(\Delta G_v\) is the driving force for crystallization i.e. the free energy difference per unit volume for the amorphous film-crystalline film transformation, and \(f(\theta)\) is a function related to the contact angle. The non-columnar structure of the BT films in the diffusion oven can be due to the faster ramp rate since the deposited films are directly placed in the already heated up furnace. This probably leads the \(\Delta G_{\text{homo}}\) for homogeneous nucleation to be surmounted due to kinetic reasons. In the RTA the films are placed at room temperature and then the temperature is raised up at the required ramp rate. The growth of columnar structure films is due to the dominance of heterogeneous nucleation over homogeneous nucleation. Schwartz et.al.\(^{125}\) have shown that PZT precursors which have
higher decomposition temperatures usually have better heterogeneous nucleation. Higher decomposition temperatures lead to reduction in the free energy for crystallization. Since this free energy difference defines the barrier height for homogeneous nucleation within the bulk of the film as well as the barrier height for the heterogeneous nucleation at the interface any change in the driving force ($\Delta G_\nu$) will impact the relative barrier heights, for these different nucleation events. In the following we apply a similar model with some modifications for alkaline earth based titanates. Addition of more and more propionate based MOD solution to the colloidal solution increases the crystallization temperature due to the presence of carbonates (Chapter 5), hence the barriers for homogeneous nucleation ($\Delta G_{\text{homo}}$) increases due to decrease of $\Delta G_\nu$. At the same time the $\Delta G_{\text{hetero}}$ can also change but the function $f(\theta)$ probably changes in such a way that $\Delta(\Delta G_{\text{homo}} - \Delta G_{\text{hetero}})$ always increases with increase of MOD solution content in the hybrid solution. This is schematically shown in the figure 7.14.

\[ \text{Fig.7.14 Hypothetical schematic depicting free energy changes with increased amounts of MOD solution in microemulsion.} \]
Microemulsion based CSD

At this point it should be mentioned that the $\Delta G_{\text{homo}}$ and $\Delta G_{\text{hetero}}$ nucleation could change for each of the hybrid solutions. In this model the $\Delta G_{\text{hetero}}$ for heterogeneous nucleation has been assumed to be constant to simplify the situation. Under a constant temperature ramp at any particular moment the greater the free energy difference between the homogeneous and heterogeneous nucleation the larger the dominance of the interface nucleation. Films with larger MOD content therefore have an increased propensity towards forming columnar grains. Further changes in ramp rates are required to get a better perspective about the nucleation events.

Therefore changes in the grain size can lead to changes in dielectric constant and tunability. Also, the high dielectric constant at such low temperatures of around 700°C can be used with base metal electrodes for the manufacture of MLCC’s. These hybrid solutions of dispersions and MOD solutions have a high potential for use in a variety of applications where films of mesoscopic thickness are required with only a few coating steps.
Chapter 8

Conclusions

8.1 Summary

In this study, deposition of various Ba-based dielectric materials have been carried out under different processing conditions and with different bottom electrodes. The results can be summarized as follows.

1. Substituted BaTiO$_3$ thin films were synthesized by chemical solution deposition methods on platinized substrates. Both A-site and B-site isovalent substitutions were considered.

   (a) Increased A-site substitution with strontium led to lower dielectric constant. Dielectric properties were found to be dependent greatly on the crystallization temperature and on the substrate. Higher crystallization temperatures of around 900°C on special substrates increased the dielectric constants by almost 30% for BST and by 100% for pure BT.

   (b) Increased B-site substitution with zirconium and hafnium led to decrease in the dielectric constant and lower the leakage of the thin films. This was explained on the basis
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of an increased Schottky barrier in the films. Optical studies performed on the Hf substituted thin films show a trend of increasing band gap with higher Hf substitutions.

2. Low temperature processing of the thin films was carried out mainly with (Ba$_{0.7}$Sr$_{0.3}$)TiO$_3$ thin films. The reason for the high temperature crystallization of BT/BST (650$^\circ$C) thin films had often been cited in the literature due to the formation of an intermediate oxo-carbonate phase. Though crystallization is evident at this temperature, usually films crystallized at 700$^\circ$C and above have good electrical properties. Such high temperatures are not feasible during conventional semiconductor processing. The following processing changes were done in order to lower the crystallization temperature or circumvent the problems encountered during high temperature processing.

(a) A more reactive atmosphere consisting of a mixture of ozone and oxygen was used to crystallize the films. At temperatures around 650$^\circ$C the amorphous films derived from the carboxylate route were found to crystallize. Though such a process did not lower the crystallization temperature, post annealing treatments in ozone reduce the leakage of the thin films by three orders of magnitude.

(b) Amorphous thin films of approximately 100 nm thickness were deposited on platinized silicon wafers and were subjected to different KrF laser fluences between 100 and 150 mJ/cm$^2$. Though the crystallinity increased with increased laser fluences, irradiation above 150 mJ/cm$^2$ led to ablation. Even with lower fluences the films were often found to be cracked. The problem of cracking was solved by keeping the substrate at an elevated temperature of 250$^\circ$C. This turned out to be a highly efficient way in reducing the substrate temperature load.

(c) The reason for high temperature crystallization of BT/BST thin films had been previously cited due to the formation of an oxo-carbonate phase when carboxylate based precursors were used. New precursor solutions based on aminoethoxides of barium and
strontium were synthesized. By use of these carboxylate free precursors the formation of the intermediate oxo-carbonate phase was avoided. This method led to lower the crystallization temperature to 600°C. Though the precursors were themselves found to decompose already at around 500°C the formation of BT/BST phase did not occur below 600°C. Absence of carbonates in the FT-IR spectra and presence of Ti-O vibrations further indicate that though TiO₂ forms at lower temperatures formation of BT is stalled till 600°C for thermodynamic reasons. Also the precursor solutions developed by this route were more stable in comparison to carboxylate based precursor solutions since possibilities of water formation by esterification are eliminated.

3. Both A-site and B-site substituted BT based thin films were fabricated on Ni electrodes. The possibility to use CSD for the deposition of thin films for future MLCC’s with thinner dielectric layers was shown. In this case carboxylate precursors were used because these precursors are commercially available and cheap. BT, BST and BTZ thin films of thickness around 600 nm were deposited by 12 coatings each. The pyrolysis and the crystallization procedures were optimized into 4 consecutive depositions followed by a crystallization step. This procedure was repeated thrice to achieve a thickness of 600 nm in 12 coating steps. Films crystallized at 1000°C had the best dielectric properties after a re-oxidation anneal due to better crystallinity and increased grain size.

4. Finally a new method of deposition of hybrid solutions based on a mixture of microemulsions and MOD solutions (µECSD) was developed. The novelty of this method lies in the fact that films of mesoscopic thickness (500 nm – 800nm) can be deposited with only a few deposition steps. As mentioned earlier, in order to deposit films of thickness around 600 nm 12 coating steps are required. With these hybrid solutions such thicknesses have been achieved with only 5-8 steps depending on the amount of the MOD solution present in the hybrid solution.
8.2 Future work

The presented research focused on processing of CSD based thin films for applications involving MLCC’s and other embedded capacitors. While the work in this thesis concentrated mostly on un-doped barium based dielectrics, future work should focus on the effect of dopants both on microstructure and electrical properties. Though there is an extensive literature available for the processing of bulk ceramic powders under various atmospheres and with various dopant concentration, literature concerning processing with thin films in this mesoscopic range on base metal electrodes under reducing atmospheres is scarce. Further optimization of the new hybrid solutions to reduce porosity of these thin films is required. Processing of these hybrid solutions under reducing atmospheres in conjunction with base metal electrodes would certainly be required. Possibilities of achieving core-shell nanoparticle structures with the microemulsions in order to attain a flat temperature coefficient of capacitance should also be investigated.
Zusammenfassung:

Im Rahmen dieser Arbeit wurden diverse Barium-basierende dielektrische Dünnschichten unter verschiedenen Prozessbedingungen und auf unterschiedlichen Unterelektroden über ein nasschemisches Abscheideverfahren (international: Chemical Solution Deposition – CSD) hergestellt und charakterisiert.

Die Ergebnisse können wie folgt zusammengefasst werden.


   (a) Der zunehmende Austausch der A-Platz Komponente Barium durch Strontium führte zu einer Abnahme der dielektrischen Konstante.

   (b) Ein Ersatz des B-Platz Kations durch Zirkonium und Hafnium führte zu einer Abnahme der Dielektrizitätsszahl bei gleichzeitiger Senkung des Leckstroms der Dünnschichten, was durch eine Zunahme der Schottky-Barriere begründet wurde.


   (a) Verwendung einer reaktiveren Atmosphäre bestehend aus einer Ozon/Sauerstoff-Mischung während der Kristallisation. Zwar konnte durch diesen Prozess die Kristallisationstemperatur nicht gesenkt werden, jedoch konnte der Leckstrom der Dünnschichten durch eine thermische Nachbehandlung in Ozon/Sauerstoff um drei Größenordnungen gesenkt werden.
(b) Amorphe Dünnschichten von durchschnittlich 100 nm Dicke wurden auf platinierten Silizium-Substraten abgeschieden und verschiedenen KrF Laserenergie zwischen 100 und 150 mJ/cm² ausgesetzt. Selbst bei niedrigen Energien wurden oft Risse in den Dünnschichten beobachtet. Zur Lösung dieses Problems wurden die auf ca. 250°C vorgeheizten Substrate mit Laser-Pulsen kristallisiert, was die Rissbildung effizient reduzierte.

(c) Bei der Verwendung von Carboxylat-basierenden Precursoren wurde als Grund für die hohen Kristallisations-Temperaturen von BaTiO₃ bzw. (Ba,Sr)TiO₃ bislang die Bildung einer Oxo-Carbonatphase genannt. Durch neue, Carboxylat-freie Precursor-Systeme basierend auf Barium- und Strontiumaminoethoxid, konnte die Bildung der Oxo-Carbonatphase vermieden werden, was die Senkung der Kristallisationstemperatur auf 600°C ermöglichte. Obwohl sich die Precursoren bereits bei 500°C vollständig zersetzen, wird die BaTiO₃ bzw. (Ba,Sr)TiO₃-Phase unterhalb von 600°C nicht gebildet. Die Abwesenheit von Carbonaten in den FT/IR-Spektren und die Anwesenheit von Ti-O-Schwingungen zeigen, dass trotz des Entstehens von TiO₂ die Bildung von BaTiO₃ aus thermodynamischen Gründen nicht stattfindet.


4. Abschließend wurde eine neuartig Methode (µECSD) zur effizienteren nasschemischen Herstellung elektrokeramischer Dünnschichten im mesoskopischen Dickenbereich (500 nm – 800 nm) vorgestellt. Hierzu werden so genannte Hybridlösungen bestehend aus einer


References


References


References


References


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