Chapter - 2
LITERATURE SURVEY

2.1 Introduction

The best facet of thin film technology is the structure formation with self sorting as one by one atom at a temperature far from thermodynamic equilibrium; this makes the synthesis of thin films a controlled process and produces meta-stable phases, artificial assemblies, multi layer and nano composites. Development of scientific awareness on preparation, structure formation, structural properties and advances in technology are the reason behind a prominent role of thin films, for the drastic improvement of new active and passive devices.

These led to the highly advanced factual art in the area of thin films which is given by a practical set of socioeconomic benefits and made thin films as emerging field of science JE Greene [28]. Enormous publications dealing with thin films are available and it is impossible to site them all in the present context. The best efforts are put forth to concise the important results at one place specially related to perovskite thin films lead zirconate titanate (PZT).

The interest of researchers aroused on thin films at the end Davisson and Germer observed electron diffraction on thin films in 1927 and in 1930 these films were applied practically in surface mirrors that have high reflectivity and on insulating substrates.

In 1940 vacuum thin film techniques and electron microscopes were developed, that supported the thin film studies. In 1970, high resolution surface imaging, analytical TEM, CVD, MBE and computer simulation atom by atom were put forward. In 1980 atomic resolution surface imaging techniques like STM, AFM, atomic layer epitaxy, and electron energy loss analysis-scanning TEM was investigated. Aberration corrected ultra high resolution analytical TEM and in situ techniques like STM and synchrotron were invented. All these inventions related to thin films have given an enormous chance to focus on thin film technology and applications.

The perovskite structure materials have attracted much interest due to their simple crystal structure that provides an understanding of the interaction between structural changes and physical properties. As the highlighting behavior unique from others, in perovskites, there is no oxygen frame work in the close-packed form. This releases the flexible path for substitution of chemicals. Due to this advantage the devices can be tailored in view of needs of industry. Here various chemical anatomy and symmetries of crystals provide a wide range of physical properties.

The diverse functionality of materials is required to design application oriented devices. The behaviors like ferromagnetic, semiconductor, superconductor, ferroelectric and ferromagnetic structures can be designed using thin films.

2.2. Review on PZT Thin Films

Lead Zirconate Titanate (PZT) comes under materials that possess many properties in built and a captivating material that has both behaviors of ferroelectricity and ferromagnetism. PZT is an interesting material of the class of perovskites for the last five decades. In 1970, T Masao [29] studied the poling temperature effect on the piezoelectric activity of metal oxide doped lead zirconate titanates. The impurities divided into three groups and the variation in piezo activity was explained by the effect of space charge generation by the addition of impurities.

In 1974, Snow [30] observed porosity elimination in Pb (Zr, Ti)O_3 ceramics by liquid phase sintering. In 1975, S Shirasaki, et al. [31] studied a range of ferroelectric substances of type $Pb_{1-x}TiO_{3-x}$ or $Pb_{1-x}Na_yTiO_{3-x+(y2)}$ with perovskite structure prepared by simple solid state reaction. The imperfections in materials are studied in terms of in-homogeneously distributed vacancies. In 1976, M Oikawa, et al. [32] studied the ferroelectric and dielectric anomaly of thin films on fused quartz and stain fewer steel substrates.

In 1977, A. Okada [33] fabricated transparent lead zirconate–lead titanate (PZT) thin films by RF diode sputtering on platinum, fused quartz, and In_2O_3 coated fused quartz. The perovskite structural formation was dependent on temperature. Ferroelectric parameters were calculated for these films.

In 1988, SK Dey, et al. [34] discussed the PZT and PLZT thin films as a function of hydrolysis water and precursor reactivity on pyrolysis behavior, cracking tendency and microstructure. In 1989, SL Swartz [35] studied the substrate dependent crystallization of PZT thin films on alumina, fused silica and silicon substrates.

In 1990, SK Dey, et al. [36] outlined the crucial physiochemical issues that bother the reproducible designing of PZT thin-films. The high field behavior, low field switching and stability behaviour of PZT thin-films were focused for radiation hard and non volatile memory applications. They also discussed the related data of these integrated films on solid Pt and sputtered Pt layer on silicon-nitride GaAs substrates.

In 1990, CJ Chen, et al. [37] talked about the asymmetric ferroelectric hysteresis loops formed by thin $Pb(Zr_xTi_{1-x})O_3$ films fabricated by sol-gel method and attributed the mechanism to the potential difference at the interface related to ferroelectric and the semiconductor is compensated by space charge. WH Shepherd [38] reported the typical fatigue and aging behaviour of sol gel deposited PZT thin films and found that neither fatigue nor aging are temperature dependent and make identification of these physical processes difficult.

BM Melnick, et al. [39] had reviewed regarding the application of sol gel process for coating PZT thin films, in order to determine device oriented fabrication process. The qualities of thin films were characterized by using various analyses. KC Chen, et al. [40] discussed the deposition of PZT films on fused silica substrates, by multiple dipping-firing processes from a stable solution of titanium isopropoxide, zirconium n-propoxide and lead 2- ethylhexanoate. X-ray diffraction analysis revealed that crystallization of amorphous film to perovskite phase is a transition through Pyrochlore phase in which nucleation is dominated.

In 1990, SA Myers, et al. [41] examined three different film compositions of PZT phase diagrams produced using organo metallic sol gels sintered using semiconductor processing techniques using transmission electron microscopy (TEM). For two compositions, of grown PZT films the perovskite structure was found in large rosettes surrounded by the polycrystalline pyrochlore phase. In $Pb_{1.1}$ $(Zr_{0.25}Ti_{0.75})O_3$ sample, only perovskite grains are there pyrochlore phase is absent here. The effect of annealing temperature-time combinations is studied for PZT thin films annealed through rapid thermal annealer (RTA).

The ferroelectric and dielectric properties of thin films were enhanced due to RTA, J Chen, et al. [42]. Y Xu, et al. [43] reviewed the built-in features and the recent achievements in the promising sol gel method for growth of ferroelectric thin films, Epitaxial growth, symmetric and also asymmetric ferroelectric hysteresis loops, heterojunction effect related to film and substrate etc. were discussed.

S-i Hirano, et al. [44] have grown $Pb(Zr,Ti)O_3$ films with preferred orientation on MgO (100), $SrTiO_3$ (100) without cracks on $Pt/Ti/SiO_2/Si$ substrates by applying metal alkoxide solutions. For early crystallization of perovskite PZT at low-temperature, the precursor films were calcinated in a H_2O-O_2 gas mixture which found to be advantageous for obtaining preferred orientation.

SJ Lockwood, et al. [45] succeeded in optimizing, PZT thin films used for CMOS integrated circuits in terms of the microstructure and ferroelectric properties. These can be used as 256 bit ferroelectric non-volatile memory devices. As the solution chemistry affects the ferroelectric properties, a 10-factor screening is used to identify water volume, solution concentration and injecting acetic acid.

CK Kwok, et al. [46], found a dramatic change regarding electrical properties of PZT thin films synthesized by modified precursor preparation method for sol-gel processing. The order of precursor mixing was changed and processing parameters have been optimized to produce high quality thin films and better electrical properties.

The impact of pyrolysis, post-pyrolysis thermal treatments, and excess lead are made clear by KG Brooks, et al. [47]. The kinetics of amorphous-Pyrochlore-perovskite crystallization are affected by using post-pyrolysis oxygen anneals at a temperature of 350–450°C. Before annealing the oxygen and lead valence in the amorphous films are greatly influenced by pyrolysis temperature. Such manipulations in the Pb valence state influence the stability of transient Pyrochlore phase and kinetics of perovskite crystallization.

A Tsutomu, et al. [48] detected the efficient means of producing smooth PZT films by focusing on factors like excess of lead, Rapid Thermal Annealing (RTA), buffer layer and preparation of crystal nucleus on the substrate. They observed rosette crystal structure as perovskite for PZT (52/48)] films prepared by sol-gel method on substrates Pt/Ti/ SiO_2 /Si. Lead deficiency in the non-perovskite phase caused by lead diffusion into the bottom electrode was detected by Energy Dispersive X-ray Spectroscopy and Auger Electron Spectroscopy.

A Kazushi, et al. [49] investigated the fatigue mechanisms of sol-gel derived PZT thin films and the effect of La on them. The result indicates that domain pinning is the dominant fatigue mechanism for PZT(40/60) and PZT(53/47). For PZT(70/30), P_r was almost constant and E_c increased with switching cycles. The addition of La even though reduced the space charge in PZT(53/47) film it could not improve fatigue characteristics.

K Udayakumar, et al. [50] fabricated ferroelectric lead zirconate titanate thin films of composition at Morphotropic phase boundary using sol gel spin coating technique. The electrical and dielectric properties were temperature and thickness dependent. Various methods of deposition routes are available for coating of thin films. out of which four different processes that include sol gel or metallorganic deposition are well established by M Sayer, et al. [51]. They reviewed the necessity and criteria for successful processing and stoichiometric volume considerations.

D Sporn, et al. [52] discussed how the sol gel processing is employed for the last 10 years to prepare perovskite films, especially PZT. They made an attempt on optimizing the thin films properties in terms of fundamental understanding of processing conditions, stoichiometry and thermal treatment. As functional properties are influenced by crystallization, specific examples are provided to explain how the thermal ramp and thickness of film greatly affect the structural evolution of the deposited thin films.

Y Liu, et al. [53] found the dependency of texture development on the temperature used during deposition especially at low regions on PZT (40/60) sol-gel thin films. The formation of (111) PZT texture is attributed to nucleation-control and solid-phase epitaxy whereas, the surface energy was minimum for the (100) phase oriented grains.

A Wu, et al. [54,55] prepared pure perovskite films at low temperature on alumina substrates. The seeding effects and crystallization behavior were carried out using XRD and SEM analysis, this conformed considerable improvement of crystallization at lower temperatures when PZT seeds were added to the sols.

RW Schwartz, et al. [56], fabricated Lead zirconate titanate (PZT 40/60) thin films on using chemical solution deposition on silicon wafers. Different chelating agents were added for this precursor solution example is acetic acid and acetyl acetone. The electrodes were coated on the films to study the electrical properties. The microstructure of films was studied using columnar growth morphology confirmed the dependency of pyrolysis temperature on the chelating agent. They explained the reason behind the change in crystallization which is influenced by driving force. The way it makes an impact on the microstructure of film based on subsequent variations that happened to be in the barrier heights for the interface (lower electrode) and surface nucleation.

The dependency of crystal orientations of lead zirconate titanate films on drying temperatures was investigated by CJ Kim, et al. [57]. Before the final treatment, the TG/DTA and FTIR spectroscopy were used to detect the remnants of organic materials related to the thin films. The relation between film orientation and residual organic content has been focused.

S-H Kim, et al. [58] Prepared sol-gel spun-casted $Pb(Zr_{0.52}Ti_{0.48})O_3$ thin film with Al_2O_3 buffer layer along with $PbTiO_3$ seed layer at a temperature of 550°C. The large nucleation sites presence influences, $PbTiO_3$ seed layer between the Pt bottom electrode and the PZT thin film. Due to this perovskite formation at low temperature was easily possible. The dielectric and ferroelectric properties were enhanced due to the presence of buffer and seed layers.

The effect of annealing time on transient intermetallic phase Pt_3Pb of PZT thin films was found by Z Huang, et al. [59], which initially increases based on annealing time and decays after reaching a maximum. Here ‘n’ is the Avrami coefficient, ’k’ is the growth rate which is determined from simulated curves.

X Fu, et al. [60] prepared Zr-rich lead zirconate titanate thin films of ratios PZT 80/20, PZT 85/15, PZT 70/30 on (1 1 1) Pt-coated Si substrates with sol–gel process using rapid thermal annealing (RTA) at 700°C for 200 s. The rock curve measurement and XRD results reveal that PZT 80/20 and PZT 85/15 have a single (1 0 0) orientation with the rocking curve FWHM of around 0.5°. The dielectric properties were dependent on preferential orientation.

XJ Meng, et al. [61] used zirconium nitrate as a substitute for Zr-alkoxides to enhance the stability of precursor solution. A highly (1 1 1) oriented PZT 50/50 thin films were formed at a low annealing of 550°C with this modified precursor solution. These films show well saturated hysteresis loops and good dielectric properties. A review of thin films applied to the micro electromechanical system was provided by Muralt. The device selected for this review is $PbZr_xTi_{1-x}O_3$ (PZT) films and an explanation were provided like how these are used in ultrasonic micro motors by P

Muralt [62]. The figures of merit for various applications are presented in view of published data.

N Sriprang, et al. [63] developed a triol influenced system for the PZT thin films. The NMR spectroscopy confirmed that the gel consists of metal ions and bound 1,1,1-tris hydroxymethyl ethane, acetylacetonate, and acetate residues, with few M–O–M bridges.

J-K Yang, et al. [64] found that the crystallization behavior and ferroelectric properties of PZT thin films are closely influenced by more lead content. Among these films with different excess amounts of Pb, the film with a surplus of Pb content has more nuclei and small grain size compared to the films of low Pb content. A depth profile analysis using Auger electron spectroscopy reveals that excess Pb enhances the formation of Ti-rich PZT at the Pt/PZT interface. With an excess of lead, the permittivity enhances and this phenomenon states that for the films coated with the low lead content solution, the oxygen vacancy accumulation supports the space charge layer formation at the easy rate.

Thin films of PZT with thickness 1.8–2.0 µm were coated on $Pt/Ti/SiO_2/Si$ substrate using excimer laser ablation by W Zhan-Jie, et al. [65]. By adding 20% surplus of lead a better crystallization at an easy rate can be expected for PZT films. Here the annealing times of 90 minutes are selected with the temperature being 750°C. The remanent polarization, coercive field and dielectric loss tangent were calculated for these films.

J-K Yang, et al. [66] attained PZT with Zr/Ti=40/60 films of different grain size of 110 and 370 nm on $Pt/SiO_2/Si$ substrate by taking care of atomic composition and annealing time. Switching cycles were used to affect the polarization of films. This, in turn, was observed to depend on grain size. As a well know fact sol–gel method is to be the best route for the production of PZT thin film materials with high quality.

The influence of acetyl acetone ligands on pyrolysis temperature to form PZT films of pure perovskite phase was discussed by L Weng, et al. [67]. A piezoelectric $PbZr_{0.52}Ti_{0.48}O_3$thin film was prepared on a micro-machined SOI wafer by sol-gel method and the dependence of output voltage of diaphragm and cantilever on sonic frequency was examined by S Murakami, et al. [68]. An attempt has been made to develop micro sonic sensors of high quality factor using piezoelectric diaphragm and cantilever. This can be used to detect special sonic waves that are emerged out during working of rotaries such as turbines, motors and engines. The estimated resonant frequency was comparable to the commercial bulk ceramic sensor.

The precursor solutions of PZT were modified with Poly(ethylene glycol) (PEG) additives of different molecular weights by S Yu, et al. [69] and PZT films were coated. The observations reveal that PEG eliminates the cracking of films due to multiple pyrolysis treatments. The young’s modulus decreases and dielectric constant increases with increase in molecular weight.

A Wu, et al. [70] reported about the nucleation stages in the growth and texture formation of perovskite PZT 52/48in the form of seeded and unseeded films. These parameters depend on seed and unseeded stages and even the pyrolysis temperature of perovskite phase formation also depends on seed layers. Low temperature heat treatment of seeded PZT films is well suited for coating on to glass, metallic or polymeric substrates.

The residual stress was significantly reduced with the inclusion of PEG to the precursor solutions by K Yao, et al. [71] for the $Pb(Zr_{0.52}Ti_{0.48})O_3$ films prepared by a modified sol-gel process. The residual stress is further decreased when the molecular weight of PEG additive is increased and these results explain the reason behind the thicker, crack free films.

I Boerasu, et al. [72] Manufactured Metal Ferroelectric Metal (MFM) structures by sol–gel deposition of a PZT at Zr/Ti =65/35. These coatings were made on various substrates along with electrodes to study the ferroelectric, dielectric and normal electric parameters. The related measurements explain that at times semiconducting properties try to dominate the ferroelectric versions of thin films to provide better applications of these in the electronic industry.

The influence of transformation temperature on preferred orientation and properties of lead zirconate titanate films with a composition near the MPB were fabricated on platinum or Si substrates using sol-gel method were studied by W Gong, et al. [73]. The PZT films pyrolysed and then annealed at different temperature to obtain (100) orientation (111) orientation. PVP assisted, films without cracks and in mono phase using PZT, $BaTiO_3$ and other combination of barium were coated as films with thickness from 2 -4 μm via non-repetitive spin-coating by H Kozuka, et al. [74]. The P-E hysteresis loop and dielectric parameters were estimated.

The chemical solution deposition of PZT 53/47 thin layers on silicon is found to shrink and developed stress with applied heat. RJ Ong, et al. [75] reported results on shrinkage and stress as determined static ellipsometry and laser reflectance respectively in a limited temperature of 700°C. This experiment provides information about densification, thermal analysis, pyrolysis and crystallization. This also gave an idea about related stress enhancement as a function of the layer by layer build up of films.

S Seifert, et al. [76] reported the dielectric and electromechanical behaviour of PZT (53/47) films on various metallic substrates were analyzed. These properties were strongly dependent on thickness. These properties like dielectric and electromechanical were described by a process imagining an interface layer between substrate and PZT film. O Sugiyama, et al. [77], used X-ray photoelectron spectroscopy (XPS) for the analysis of crystalline phase and constituents of we chemical deposition based lead zirconate titanate thin films. From the calibration equations, it is possible to estimate the composition of the sample in concern. The surface layers were having a thickness of tens of nm and compositionally, crystallographically different from inside. These results were conformed using energy dispersive X-ray spectroscopy.

Lead zirconate titanate derived as thin films on multi coated substrates using hybrid growth techniques i.e. the films were coated using two different methods. One among them is chemical deposition and the other is physical deposition method by ZJ Wang, et al. [78]. The films had an overall perovskite structure without Pyrochlore phase and the HTEM image depicts that the coatings were continuous with the identical orientation of crystallites for both methods of deposition.

Q-M Wang, et al. [79] realized that it is difficult to control the orientation and cross section of PZT material coated thin-films. This statement is given after ample trials to prepare coatings that suit the desirable application areas such as ceramic and mechanical fields. Even after adopting the best possible methods to study the required properties the parameters were definitely dependent on possible orientations.

TA Berfield, et al. [80] investigated piezoelectric properties of three different samples of $Pb(Zr_{0.53}Ti_{0.47})O_3$ thin film derived using sol gel method. These samples were integrated on to $Pt/Ti/SiO_2//Si$ substrates to portray the effect of residual stress on the different thickness relied processes. Residual tensile stresses and field induced strains were determined from wafer curvature measurements. The interferometer is used at either large AC driving voltage or at small AC ripple voltage compared to prescribed range values of dc biases.

Z Chen, et al. [81] studied in a definite order the effect of concentration of Pb precursor, seeding layer along with other possible seeding layers on the crystalline orientation of lead zirconate titanate films fabricated using sol–gel process. The orientation of the films definitely depends on a number of precursors used. Based on the high volatile property of lead always an excess is used during gelation. Here it is noted that the percentage of excess lead added to the solution determines the properties of the material under study.

The electromechanical coupling coefficient is determined for piezoelectric membranes of a 2d structure consisting of a lead zirconate titanate PZT stack on the silicon were studied experimentally by J Cho, et al. [82]. For variation in PZT size, thickness of the substrate, stress, side length and electrode coverage are noted to be influencing parameters. In view of this, it was observed that the residual stress plays a dominant role on the magnitude of the electromechanical coupling coefficient. These results are guidelines for piezoelectric membrane designers. A study made by S Yang, et al. [83] on a silicon substrate made them grow films in amorphous and also polycrystalline forms.

N Izyumskaya, et al. [84] discussed the technological issues related to growth, processing and various physical properties and application areas of lead-zirconate-titanate in the form of fine coatings. The PZT is given special focus due to its large electromechanical constant, saturation polarization and dielectric constant.

Thin films with a wide range of Zirconium/Titanium ratios were derived from the precursor of the metal alkoxide. These were deposited on platinised silicon substrates by using wet chemical deposition method, by P Khaenamkaew, et al. [85]. Zr/Ti ratio of 52/48 exhibits the most prominent properties including high remanent polarization, low coercive field and excellent dielectric properties.

T Schneller, et al. [86] have used various alkoxides made of transition metals and carboxylates of lead for preparing Tetragonal $Pb\ (Zr_{0.3}Ti_{0.7})O_3$ films on platinised silicon wafers by chemical solution deposition. Increasing ambient humidity after the spin coating process produces a significant deterioration in the final film properties on a copper substrate. This was explained in terms of a retarded formation of the (111) texture.

Because of the volatility of PbO, the PZT becomes incompatible with base metal technology. To overcome this, MD Losego, et al. [87] strategically designed three solution chemistries. They also designed various processing conditions to overcome interfacial reaction without oxidizing the base metal or cracking the film. They found solutions of acetic acid as most compatible with the processing constraints to coat the PZT films on a copper substrate.

Z Jiao, et al. [88] injected charges in to PZT thin films and then electric force microscopy was used to observe the charge storage and transportation through the films. These properties support for the films to be used in microelectromechanical devices. Substrate dependent structural and ferroelectric properties were studied for sol gel derived PZT thin films on stainless steel and on a platinum-coated silicon substrate (Pt/Si) by V Stancu, et al. [89]. The results gave a path to use minimum cost substrates like stainless steel for epitaxial growth of films. The films with different thicknesses were prepared on platinum/Titanium/Silicon substrates of various orientations using sol–gel method by A Bhaskar, et al. [90].

The films were made to anneal at 450°C for half an hour using a cavity of single-mode using high frequency microwaves. Perovskite phase formation happened at a thickness of 166nm where the grain size increases, the surface roughness was decreased. Microwave annealing was effective to obtain low temperature crystallization and provide better ferroelectric and surface properties.

A Chowdhury, et al. [91] discussed the impact of isopressing of $PbZr_{0.3}Ti_{0.7}O_3$ sol–gel coated films prior to annealing on ferroelectric properties. The ferroelectric parameters varied based on compaction pressure, the variation in polarization was attributed to the balance between porosity and strain levels.

The influence of texture of film and constituents on the transverse piezo coefficient of PZT was studied by D Ambika, et. al. [92]. The films of 2.0µm thickness were fabricated on silicon substrates (111) Pt/Ti/SiO2/Si using a sol-gel spin-coating technique. PZT films coated on substrates with a strontium titanate as bottom layer have an orientation of (111) and exhibit excellent piezoelectric and dielectric properties. It is shown that films of different orientation can be gained on Pt/Ti/SiO_2/Si substrate using a sol–gel technique. Q Chi, et al. [93] found that the PZT film orientation can affect the saturation of ferroelectric hysteresis loops which happens due to in plane domain switching under externally applied field.

QL Zhao, et al. [94] prepared thick films combined with ZnO nano whiskers on Pt/Cr/SiO2/Si substrates by hybrid sol–gel method via spin-coating. High quality and good perovskite structure are observed in composite ZnOw–PZT thick films.

These are observed to exhibit good ferroelectric and dielectric properties which are comparable to PZT thick films.

The quality and structure patterning of lead zirconate titanate thin films depends on insoluble residues obtained during the wet etching process. L Che, et al. [95] introduced a single step wet etching process for thin films, using the buffered solutions of HF and nitric acid for patterning films for microelectromechanical system (MEMS) applications.

The effect of the annealing holding time on dielectric as well as ferroelectric properties of PZT thin films on Pt/Ti/SiO_2/Si substrate was investigated by F Chengju, et al. [96]. The annealing maintenance time influenced the damping property of epoxy/PZT film/epoxy sandwich composites.

P Jegatheesan, et al. [97] deposited PZT films at MPB on bare Si and ZrO_2/Si substrates using sol gel spin on technique. The effect of step by step crystallization based microstructure, thickness, ferroelectric and dielectric properties of PZT thin films has been studied. The said properties were enhanced with step by step crystallization.

Structural changes related to excess lead content in initial solution were observed for PZT thin films by AS Sigov, et al. [98] using Transmission Electron Microscopy (TEM). The variation of lead content was in the range of 5 to 50 mol% and PZT films were coated on Si-SiO_2-Ti-Pt using sol gel technique.

Pure and doped Pb $(Zr_{0.53}Ti_{0.47})O_3$ thin films were calcined at 700ºC in Pb rich atmosphere for two hours by M Benam [99]. For these films negligible effect occurs during tetragonal–rhombohedral transition and the optimal amount of electrical and dielectric parameters were obtained. For sol gel deposited PZT thin films without any change in heat treatment conditions such as temperature, ramping rate, and annealing time, the films grain size was varied by adding a small amount of organic additive to PZT sol-gel solution for a control of nucleation to form PZT oxide by T Noguchi, et al. [100]. The conductivity of oxygen vacancies is suppressed by fabricating interfaces with the multi-annealing process, parallel to film surface with the grain size greater than film thickness.

The thin films annealed with in situ LASER system show well saturated hysteresis loops and loss tangents on LASER crystallized "$Pb(Zr_{0.20}Ti_{0.80})O_3$" seed layer, by A Rajashekhar, et al. [101]. D Toshihiro, et al. [102] investigated the role of PVP as a stress- relaxing agent in suppressing crack generation during fabrication of PZT thin films. Based on young's modulus values at different temperatures, it was confirmed that as PVP suppress crack formation, the young's modulus was degraded.

H-J Tseng, et al. [103] presented the development of tactile sensors based on PZT thin films which are used to measure human pulses at carotid, finger, radial artery and apical regions. The PZT thin-films deposited using sol gel process and annealed to 650°C for 10 minutes. These thin films were characterized by their sensitivity in the range of 0.798 mV/g.

N Bassiri-Gharb, et al. [104] reviewed the Chemical solution deposition (CSD) methods for processing of thin and ultrathin ferroelectric films, and high aspect ratio ferroelectric nanostructures. This method gives a low-cost, versatile approach for PZT and barium titanate.

The thin films were coated using sol–gel method and crystallized by microwave irradiation at 2.45 GHz by YN Chen, et al. [105]. They found that during initial crystallization an initial phase is formed with perovskite crystal structure but had smaller lattice constant than actual perovskite PZT. According to Chen et al, this middle phase acts as a nucleation site for the perovskite PZT and grew as a columnar grain structure and confirms the effect of microwave irradiation on crystallization.

The effect of Ti and Zr alkoxides in 2-methoxyethanol on electrical properties of PZT films prepared on platinized silicon substrates via chemical solution deposition was studied by NM Kotova, et al. [106]. The electrical properties were best when zirconium n propoxide was used. The effect of annealing duration on pure perovskite formation of PZT thin films (Zr/Ti: 53/47) prepared by sol–gel method was studied using FESEM analysis by R Laishram, et al. [107]. With the rise in annealing duration, the Pyrochlore phase disappears and at 1 hour of annealing time pure perovskite phase forms. $PbZr_{1-x}Ti_xO_3$ (PZT) thin films are synthesized with Zr/Ti ratio close to tetragonal–rhombohedral phase boundary which happens at x = 0.48 due to its high electro-mechanical coupling at this composition.

Q Liu, et al. [108] studied the epitaxial growth and electrical properties of PZT (Zr/Ti = 52/48) thin films with a thickness of 30 nm to 65 nm on Nb-doped $SrTiO_3$. M Bayraktar, et al. [109] reported epitaxial growth of PZT films of (100) and (110) orientation by utilizing $Ca_2Nb_3O_{10}$ (CNO) and $Ti_{0.87}O_2$ (TO) nano sheets as crystalline buffer layers. Fatigue measurements gave stable ferroelectric properties of these films and (100) oriented PZT films on CNO nano sheets show a large remanant polarization.

TD Cheng, et al. [110] fabricated perovskite PZT thin films on FTO coated glass substrate. It was used as a buffer layer and the bottom electrode. These sandwich-structure Au/PZT/FTO capacitors had excellent transmittance, ferroelectric and leakage properties with the remanent polarization of about 56 $\mu C/cm^2$. W Wang, et al. [111] described the effect of different heat treatment processes on the microstructure and orientation of PZT thin films suitable for micro actuators. M Zhu, et al. [112] investigated strong optical and electro-optic anisotropy in ferroelectric $Pb(Zr_{0.48}Ti_{0.52})O_3$ thin films epitaxial grown on Nb-$SrTiO_3$ (001), (011), and (111) substrates using magnetron sputtering.

Masruroh, et al. [113] built highly crystalline crack free PZT thin films on a silicon wafer with a composition near to Morphotropic phase boundary Pb/Zr/Ti: 100/50/50 by varying sol concentration and rotational speed in the spin coating process. The concentration of sol is varied by adding proponol of 1, 3 and 5 ml. The XRD, SEM analysis indicates fineness, flatness, and homogeneous films.

MT Ghoneim, et al. [114] utilized the inverse proportionality relation between substrate thickness and flexibility to design $Pb_{1.1}Zr_{0.48}Ti_{0.52}O_3$ (PZT) thin films for ferroelectric random access memory (FeRAM) on silicon, preserving the high performance of CMOS electronics. The crystalline seed layer of lead titanate (PTO) was prepared using the 2-methoxyehanaol route and on this PZT (Zr/Ti 52/48) thin films were deposited by S Mhin, et al. [115]. During heating, the tetragonal to cubic phase transformation happens before perovskite phase formation and subseqent nucleation ocuurs in cubic phase in which 100 texture is dominant which is in both seed layer and PZT films.

VP Afanas'ev, et al. [116] proposed a model for the formation of internal fields at the grain boundaries of PZT films. The local distortion of stoichiometric compostion caused by segregation of oxygen and lead ions form the bulk PZT grains towards their boundaries duing firing, this gives electrical double layers near the grain boundaries and fixes polarization.

TA Berfield, et al. [117] used laser based spallation method to determine the adhesion strength of sol gel coated films on two substrates. PZT thin films spin coated on to bare Si/SiO_2 were found to have extremely high adhesion, a self assembled octadecyltricholrosilane (ODS) monolayer is coated on to Si/SiO_2 to use as the second substrate and the adhesion strengh was found to reduce signicantly.

During sol–gel synthesis to maintain target stoichiometry, the excess lead precursor is used for coating PZT films by I Gueye, et al. [118]. With 10% of excess lead surface nanostructures appear and at 30% excess lead inhibits them. SU Khan, et al. [119] studied about various processing steps involved in sol gel spin coating, and soft lithographic techniques to produce good quality and high pattern PZT thin films with high fidelity. Structural, morphological, ferroelectric and dielectric properties of these films were investigated.

The pyroelectric power density of $Pb(Zr_{0.52}Ti_{0.48})O_3$ films prepared by sol gel process on Si substate has been estimated as a function of temperature by R Moalla, et al. [120]. The intrinsic pyroelectric coefficient was measured through ferroelectric loops.

MF Rahman, et al. [121] used Isopropanol based solutions owing to their less toxic nature, for preparing $Pb[Zr_{0.52}Ti_{0.48}]O_3$ (PZT) films by sol gel spincoating method. Ferroelectric and dielectric properties were studied for homogeneous polycrystalline films coated on Gold (Au),platinum (Pt) and indium tin oxide (ITO) substrates.

A Rajashekhar, et al. [122] suggested that integration of lead zirconate titanate films on temperature-sensitive substrates will provide an easy process of growing films on substrates. This films can be grown at temperatures near to 400°C, this will benefit in terms of economy. They used in situ pulsed-laser annealing to grow crystalline $PbZr_{0.52}Ti_{0.48}O_3$ thin films at a substrate temperature of ~370°C on buffered platinized silicon. The time taken for annealing with respect to depostion found little effect on lateral grain growth.

D Wang, et al. [123] used electrohydrodynamic atomization deposition and mechanical polishing for the fabrication of dense and even PZT thick films. For this the PZT slurry was ball-milled and the optimum milling time to produce dense films was found to be 50 hours. The piezoelectric constant is found to vary before and after mechanical polishing. TF Zhang, et al. [124] calculated giant energy storage density and energy storage efficiency for $PbZrO_3$ thin films of (100) and (111) orientation which were found to depend on post annealing temperature. These results indicated that films had a potential application in energy storge devices.

G Esteves, et al. [125] used synchrotron X-ray diffraction and measured ferroelectric/ferroelastic domain reorientation for micrometer thick tetragonal (111) textured films. Results were reported for dense films clamped to the substrate, dense films partially released from the substrate and films with 3% volume porosity. The released or porous films exhibited neither significant enhancement in domain reorientation nor in lattice strain, where as same experiments on (100) films has a significant enhancement in domain reorientation in released and porous films.

H Nazeer, et al. [126] studied young’s modulus and residual stress of PZT thin films, with (110) orientation based on the resonance frequency. The growth method used was pulsed laser deposition on silicon cantilevers along 〈110〉 and 〈100〉 orientations. The mechanical parameters clearly depend on the cantilever orientation with respect to the silicon crystal and residual stress increases sharply at a composition of x=0.2 to 0.4. This variation is attributed to the difference in thermal expansion between silicon and PZT.

J Ouyang, et al. [127] demonstrated photonic sintering of aerosol jet printed Lead Zirconate Titanate (PZT) thin films on stainless steel substrates. Ferroelectric and piezoelectric properties were measured for both traditionally sintered and photonically sintered films. During photonic sintering sub milli sec pulses of high intensity broad spectrum were used repetitively with the highest substrate temperature at 170.7ºC, this enables the process to be used for low melting point substrates. The results indicate that photonic sintering PZT films exhibit superior electrical properties.

GD Shilpa, et al. [128] have reviewed the applications of $PbZr_xTi_{1-x}O_3$ ferroelectric thin films for Micro Electro Mechanical Systems (MEMS) ultrasonic sensors, using deposition techniques like sol-gel and magnetron sputtering.

R Tamano, et al. [129] investigated the effect of crystallographic orientation on the ferroelectric properties of $Pb(Zr,Ti)O_3$ (PZT) thin films grown on (111) and (100) oriented Pt substrates. The doped PXZT films prepared using chemical solution deposition had identical crystallinity but the ferroelectric properties were enhanced.

K Guo, et al. [130] fabricated biphasic magneto electric composite films of $Pb(Zr_{0.52}Ti_{0.48})O_3$ and $Bi_{0.9}Nd_{0.1}FeO_3$ on $Pt(111)/Ti/SiO_2/Si(100)$ substrates via Sol–gel and Rapid Thermal Process, which formed $Pb(Zr_{0.52}Ti_{0.48})O_3/Bi_{0.9}Nd_{0.1}FeO_3$and $Bi_{0.9}Nd_{0.1}FeO_3/Pb(Zr_{0.52}Ti_{0.48})O_3$ bilayer structures due to the different deposition sequences. These bilayer nanostructures show deposition technique dependent excellent ferroelectric and ferromagnetic properties measured using physical properties measurements systems.

J Lim, et al. [131] investigated the visible emission property of $Pb(Zr,Ti)O_3$ (PZT) thin films prepared on $Pt/Ti/SiO_2/Si$ substrates via sol gel spin coating, by irradiating with gamma-ray (γ-ray) at various total doses up to 1000 kGy. The spectrum of γ-ray-induced emission starts at 550nm which is quite narrow and different from normal defects such as oxygen vacancies. They suggested that the reason for this can be detected using low temperature photoluminescence spectroscopy.

This literature review demonstrates the great potential of the PZT thin films and provides a scope for further studies on them. The films can be synthesized using a simple method of sol gel spin coating and as it comes under multiferroic the magnetic properties can be concentrated. The studies in this direction further make PZT a potential material for device applications.