Deposition, Characterisation, and Piezoelectric Response Estimation of Strontium-doped Lead Zirconate Titanate Thin Films

A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy

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DECLARATION

I certify that except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis is the result of work which has been carried out since the official commencement date of the approved research program; and, any editorial work, paid or unpaid, carried out by a third party is acknowledged.

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Sharath Sriram
March 2009
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# GLOSSARY

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<tr>
<td>AFM</td>
<td>Atomic force microscopy (microscope)</td>
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<tr>
<td>$d_{33}$</td>
<td>Piezoelectric charge coefficient (Units: pm/V or pC/N), with values specified in this thesis for the thin films being effective values ($d_{33}^{\text{eff}}$)</td>
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<tr>
<td>EDX</td>
<td>Energy dispersive X-ray analysis</td>
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<tr>
<td>$\varepsilon_0$</td>
<td>Dielectric permittivity of free space, with a value of $8.854 \times 10^{-12}$ F/m</td>
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<tr>
<td>$\varepsilon_r$</td>
<td>Relative dielectric permittivity (constant)</td>
</tr>
<tr>
<td>$g_{33}$</td>
<td>Piezoelectric voltage coefficient (Units: Vm/N)</td>
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<tr>
<td>PSZT</td>
<td>Lead strontium zirconate titanate</td>
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<tr>
<td>PZT</td>
<td>Lead zirconate titanate</td>
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<tr>
<td>RF</td>
<td>Radio frequency</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscopy (microscope)</td>
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<tr>
<td>SIMS</td>
<td>Secondary ion mass spectrometry</td>
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<tr>
<td>TEM</td>
<td>Transmission electron microscopy (microscope)</td>
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<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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<tr>
<td>XTEM</td>
<td>Cross-sectional transmission electron microscopy</td>
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ABSTRACT

Lead zirconate titanate (PZT), in the form of both bulk and thin films, is used in most piezoelectric applications due to its high piezoelectric response coefficients. Strontium-doped lead zirconate titanate (PSZT) has shown improved piezoelectric response characteristics in bulk form. This work investigates the deposition and characterisation of PSZT with the composition $(\text{Pb}_{0.92}\text{Sr}_{0.08})(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$ in the form of thin films, and reports on results from the estimation of the piezoelectric response of these thin films using two new techniques.

The influence of RF magnetron sputter deposition parameters on the composition and orientation of PSZT thin films has been studied. Investigation of the consequence of varying the oxygen partial pressure during deposition on thin film stoichiometry, the influence of the choice of metal-coated silicon substrates on thin film orientation, and the effect of post-deposition cooling rate have been used to identify optimal deposition conditions. The existence of a modified unit cell resulting from these deposition parameters has been verified, and the resulting lattice parameters were estimated. Extensive materials characterisation (using microscopy, diffraction, and spectroscopy) of the PSZT thin films deposited on gold and platinum coated silicon substrates is reported.
The limited techniques available for quantitative estimation of $d_{33}$ for piezoelectric thin films initiated an investigation into alternative possibilities, as a consequence of which two new techniques for piezoelectric coefficient estimation, under the inverse piezoelectric effect, have been developed. One technique capitalises on the measurement accuracy of the nanoindenter in following thin film displacement, while the other uses a standard atomic force microscope in contact imaging mode to estimate $d_{33}$. The development, scope, and limitations of both techniques are discussed.

The techniques developed have been used to estimate the piezoelectric response of PSZT thin films. Depending on the thin film deposition parameters and the analysis frequency, values of piezoelectric response higher than any measured for thin films on silicon have been estimated. PSZT thin films deposited on gold-coated silicon at low deposition temperatures resulted in $d_{33}$ values up to 892 pm/V. The study of the piezoelectric response in the millihertz frequency regime resulted in colossal values (ranging in tens of thousands of pm/V) for PSZT thin films deposited at high temperatures on platinum-coated silicon. This was hypothesised to be a result of enhanced ferroelastic domain switching. This hypothesis was verified by reducing the clamping on domains by synthesising island-structured PSZT films and obtaining an increased piezoelectric response.
CHAPTER 1

INTRODUCTION

1.1 Motivation and Thesis Outline

Piezoelectric materials are suitable for a wide range of applications such as transducers, actuators, and sensors. This makes the applications of piezoelectric materials very multidisciplinary, which are as varied as drug delivery systems, nanoscale manipulation devices, and ferroelectric random access memories all of which have been demonstrated. Piezoelectric materials have also created widespread interest given their potential for incorporation in efficient energy scavenging applications, where electrical energy is generated by transforming mechanical energy prevalent in the environment in the form of vibrations (e.g. acoustic vibrations, ultrasonic vibrations, human motion, wind energy) [1.1-1.4]. To realise these applications, high performance piezoelectrics, which can be integrated into device fabrication processes, are essential.
There is a plethora of information available on piezoelectric materials and properties, based on research results from the study of bulk ceramics and pellets. While the information available on thin films of piezoelectrics is rapidly increasing, the numerous variables involved in thin film synthesis and characterisation creates room for continuing and extensive investigation.

Lead zirconate titanate (PZT) is the most researched piezoelectric material, given its significantly larger piezoelectric response and electromechanical coupling efficiency [1.5]. On focussing investigations on thin films of PZT, with the aim of incorporation into microfabricated devices, the dominant influence of deposition conditions on the quality and piezoelectric performance of these films became apparent. The addition of strontium (Sr) as an A-site dopant in the perovskite $\text{ABO}_3$ structure of PZT, to form strontium-doped PZT (PSZT), is reported to significantly enhance the piezoelectric properties of undoped PZT [1.6-1.9].

The motivation of this thesis lies in the combination of factors highlighted in the preceding three paragraphs. Given the requirements for further knowledge on the synthesis and characterisation of thin film piezoelectrics, with the potential to utilise this knowledge in creating energy scavenging technologies for the future, this thesis focuses on optimising a high performance piezoelectric in the form of PSZT. The importance of using thin films of piezoelectrics is the fact that such films enable easier integration into microfabricated devices, and most importantly allow the development of versatile designs by photolithographic means to perform energy amplification.

The work in this thesis aims to deliver optimised piezoelectric thin films as a precursor to realising silicon-based energy harvesting technology.
1.1.1 Thesis structure

This thesis has been segmented into chapters and sections which can be read as individual entities of research. This has been done to allow future readers of this work, to read it in part or in whole. The order of the chapters in this thesis follows the categories listed in the thesis title.

Chapter 2 describes results from the investigation of the influence of deposition parameters on PSZT thin film properties. The influence of oxygen partial pressure on thin film composition and structure is presented. Also, the influence of bottom electrodes chosen on resulting thin film crystallography is reported.

Chapter 3 presents results from extensive materials characterisation of the PSZT thin films. The characterisation was performed using a combination of microscopy, spectroscopy, and diffraction techniques; this was carried out on three categories of PSZT thin films.

Chapter 4 presents the development of two techniques for the estimation of thin film piezoelectric response coefficient ($d_{33}$). The techniques were developed using a nanoindenter and an atomic force microscope.

Chapter 5 presents results from piezoelectric response characterisation of PSZT thin films. The characterisation was carried out using the techniques developed in Chapter 4.

Chapter 6 summarises the results from this thesis, and proposes avenues for future research.
This thesis has three appendices: (i) Appendix A details all experimental conditions and parameters used during the thesis, (ii) Appendix B describes the first instance of deposition of a PZT compound with perovskite structure on silicon dioxide, and (iii) Appendix C reports on preliminary results from the in situ investigation of thermally influenced phase transformations in the PSZT thin films.

1.2 Publications

The following is a list comprising of publications during the course of this doctoral program. All the publications listed relate to thin film characterisation, and those relevant to this thesis are marked with an asterisk.

1.2.1 Peer-reviewed journal articles


Highlighted in online news:
http://www.newsrx.com/print.php?articleID=1391136


Cover illustration for the journal issue chosen from this article


1.2.2 Peer-reviewed conference proceedings


1.3 Original Scientific Contributions

This thesis has contributed a significant amount of information to the body of knowledge on the deposition, materials characterisation, and response estimation of piezoelectric thin films; in particular, for PSZT thin films. A summary of some of the major contributions is listed below:

A. Optimised deposition parameters for PSZT thin films, in order to attain desired chemical stoichiometry and preferential orientation.

B. Detailed microstructural characterisation of piezoelectric thin films deposited on metallised (gold and platinum coated) silicon substrates.

C. Two new techniques for the measurement of piezoelectric charge coefficient ($d_{33}$) of thin films have been developed.

D. Values of $d_{33}$ significantly larger than those reported in literature for similar films have been obtained. These high piezoelectric response values have been obtained for PSZT thin films deposited on gold-coated silicon at low temperatures and also for measurements carried out in the millihertz frequency regime for PSZT thin films on platinum-coated silicon.
CHAPTER 2

OPTIMISATION OF PSZT THIN FILM DEPOSITION CONDITIONS

2.1 Introduction

PSZT thin films were deposited by RF magnetron sputtering. Table 2.1 shows the various sputtering parameters used.

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<td>Target to substrate distance</td>
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<td>Base pressure</td>
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<td>Sputtering pressure</td>
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</table>
Sputtering parameters principally determining the deposition rate of the thin films were kept constant. These parameters (deposition power and target-substrate distance) were chosen so as to achieve a compromise between a slow deposition rate to enable grain growth and crystallisation, while achieving a reasonable deposition rate to achieve micron-thick films. Initial tests showed that the choice of forward RF power of 100 W (maintaining the reflected power at ~0 W) and a target-substrate distance of 70 mm, resulted in a deposition rate of 300-400 nm/hour. This variation is over 3-inch substrates due to the absence of substrate rotation option in the sputtering system. This deposition rate was considered satisfactory to achieve micron-thick films, and as a result these parameters were kept constant during further study. Sputtering parameters such as post-deposition cooling rate, sputtering pressure and substrate temperature which are expected to have a significant influence on the composition, crystal structure, and microstructure of the thin films were varied during this study.

2.1.1 Influence of post-deposition cooling rate

In the months preceding the start of this doctoral program, the influence of this single parameter was studied. For this reason, this discussion is brief and is included only in this sub-section. While the substrate temperature during deposition is a critical variable in determining the crystallography of these complex perovskite-structured PSZT thin films (the influence of which is discussed in Section 2.3), post-deposition thermal processing was expected to influence the degree of grain growth and crystallisation. This work found that slower post-deposition cooling results in thin films exhibiting more pronounced perovskite structure. The optimal post-deposition cooling rate was 5 °C/min. This was also found to be better than post-deposition annealing, which resulted in microcracks in the thin films. A detailed description of this study is presented in [2.1].
2.2 Influence of Oxygen Partial Pressure

The level of piezoelectric response exhibited by PZT compounds depends on the thin films having a composition closely corresponding to the ideal $ABO_3$ structure and on having a preferential perovskite orientation. Lead loss and lead excess have been reported to have a marked influence on the materials properties of PZT type compounds [2.2, 2.3], with the composition variations affecting perovskite orientation.

Deposition of PSZT thin films was carried out in an atmosphere of 10% oxygen in argon. Argon is an inert gas and exerts no influence on thin film composition. Changes in sputtering pressure are directly related to changes in the partial pressure of oxygen present in the sputtering environment. This section reports on the influence of the oxygen partial pressure on the chemical composition, crystal structure, and surface morphology of the deposited PSZT thin films. Deposition was carried out on platinum-coated silicon substrates at 650 ºC – the substrate temperature was kept constant to study the influence of partial pressure. The results obtained from films deposited at oxygen partial pressures of 1, 2, 3, 4, and 5 mTorr (relating to sputtering pressures from 10-50 mTorr) are discussed.

2.2.1 Composition analysis

X-ray photoelectron spectroscopy (XPS) analysis was carried out to study the composition variations in the PSZT thin films deposited at varying oxygen partial pressures. Peaks for lead, zirconium, titanium, and oxygen expected at around 137 eV, 181 eV, 454 eV, and 531 eV, respectively, were observed. Examples of the spectra recorded are shown in Fig. 2.1. Peaks for the dopant (strontium) were not pronounced due to its low concentration, and possible detected peaks at ~133 eV for strontium could not be resolved satisfactorily due to their vicinity to the peaks of lead.
Figure 2.1: XPS spectra for PSZT thin films deposited at sputtering pressures of 10, 20, and 30 mTorr. The spectra for 10 mTorr and 30 mTorr overlap, corresponding to the similar stoichiometries estimated. (Also see Table 2.2)

XPS analysis highlights the marked influence of variations in oxygen partial pressure during sputtering, observed by variations in oxygen (O) concentration in the thin films, and in some cases by the undesirable decrease in lead (Pb) concentration in the thin films (Table 2.2). Films deposited at sputtering pressures of 10 and 30 mTorr (oxygen partial pressures of 1 and 3 mTorr, respectively) have resulting compositions which are acceptably close to the PSZT 8/65/35 stoichiometry of the sputtering target. The composition of films deposited at sputtering pressures of 20 mTorr and 50 mTorr indicates insufficient and excess lead, respectively. The zirconium (Zr) to titanium (Ti) ratio of films deposited at 10, 30, and 40 mTorr was reasonably constant (the ratio varying between 1.90 and 2.15), while the lead and oxygen content varied relative to the other. As can be observed from Table 2.2, the films deposited at 10 mTorr appears to have the composition closest to the desired $ABO_{3}$, albeit mildly lead deficient.
Table 2.2: Variations in composition of PSZT thin films with sputtering pressure.

<table>
<thead>
<tr>
<th>Sputtering pressure (mTorr)</th>
<th>O₂ partial pressure (mTorr)</th>
<th>Pb (%)</th>
<th>Zr (%)</th>
<th>Ti (%)</th>
<th>O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1</td>
<td>18.18</td>
<td>14.72</td>
<td>7.73</td>
<td>59.36</td>
</tr>
<tr>
<td>20</td>
<td>2</td>
<td>12.80</td>
<td>17.94</td>
<td>9.19</td>
<td>60.08</td>
</tr>
<tr>
<td>30</td>
<td>3</td>
<td>22.21</td>
<td>14.28</td>
<td>6.81</td>
<td>56.70</td>
</tr>
<tr>
<td>40</td>
<td>4</td>
<td>25.83</td>
<td>14.23</td>
<td>6.63</td>
<td>53.24</td>
</tr>
<tr>
<td>50</td>
<td>5</td>
<td>26.41</td>
<td>13.14</td>
<td>5.40</td>
<td>55.05</td>
</tr>
</tbody>
</table>

The trend observed in the composition (with the exception of films deposited at 20 mTorr) agrees with earlier studies on diffusive transport regime assisted deposition of heavier atoms [2.4, 2.5]. With increasing sputtering pressure, lighter atoms experience more collisions (with decreased mean free path), as a result of which the deposited films become richer in the heavier species which constitute the film. A combination of the previous studies on transport regimes during sputtering and the results presented here provide a technique for optimising lead content (by altering the sputtering pressure) in lead-based or PZT-type films, where lead-loss during sputtering often occurs, resulting in poor electrical performance.

2.2.2 Crystallographic orientation analysis

Glancing angle X-ray diffraction (GA-XRD) has been used to study the crystallographic orientation of the deposited PSZT thin films. PSZT film peaks in diffractograms obtained using Bragg-Brentano XRD were over-shadowed by substrate peaks; this was overcome by using GA-XRD. All deposited thin films were polycrystalline with preferential orientation(s). Figures 2.2(a) and 2.2(b) show expected perovskite peaks at 2θ of 29.6° and 34.3° and these correspond to (104) and (006) orientations for a rhombohedral PSZT unit cell [2.6]. Figure 2.2(c) shows another expected peak for PSZT thin films corresponding to the (108) orientation. The relative
shifts of the perovskite peaks with respect to variation in oxygen partial pressure are evident in the diffractograms shown in Fig. 2.2. Films deposited at 10 and 30 mTorr, and which show similar composition, show similar orientation and least variations from expected 2θ positions. High levels of lead (as in films deposited at 50 mTorr) results in an increase in the exhibited d-spacings which has caused the peaks to shift left. High levels of oxygen (as in films deposited at 20 mTorr) results in a decrease in d-spacing from expected values which has caused the peaks to shift right. This result corresponds well with the radius of the atoms, with lead having a larger atomic radius than oxygen.

Figure 2.2: Comparison of glancing angle X-ray diffraction results for PSZT thin films deposited under different sputtering pressures. Parts (a-c) of the image show significant 2θ positions for PSZT.

2.2.3 Surface morphology analysis

The surface morphology of PSZT thin films deposited at different oxygen partial pressures has been analysed using atomic force microscopy (AFM). The average surface roughness ($R_a$) values and grain sizes measured are listed in Table 2.3. An AFM scan of a PSZT thin film deposited at 10 mTorr is shown in Fig. 2.3(a); these films had the least surface roughness and had uniformly sized grains. Figure 2.3(b) shows
an AFM scan of a PSZT thin film deposited at 30 mTorr illustrating the presence of crystalline agglomerates. Films deposited at 20 and 50 mTorr were similar to this, also with crystalline agglomerates. Films deposited at 50 mTorr contain the maximum amount of lead, and are extremely rough. The observable effect that composition had on orientation is not apparent in the case of the AFM results, with no obvious trend being present in this case.

Table 2.3: Average surface roughness ($R_a$) and grain size of PSZT films deposited under different sputtering pressures.

<table>
<thead>
<tr>
<th>Sputtering pressure (mTorr)</th>
<th>$O_2$ partial pressure (mTorr)</th>
<th>$R_a$ (nm)</th>
<th>Grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1</td>
<td>10.93</td>
<td>170</td>
</tr>
<tr>
<td>20</td>
<td>2</td>
<td>44.82</td>
<td>170</td>
</tr>
<tr>
<td>30</td>
<td>3</td>
<td>37.04</td>
<td>140</td>
</tr>
<tr>
<td>40</td>
<td>4</td>
<td>19.80</td>
<td>210</td>
</tr>
<tr>
<td>50</td>
<td>5</td>
<td>43.93</td>
<td>140</td>
</tr>
</tbody>
</table>

Figure 2.3: AFM contact mode $5 \, \mu m \times 5 \, \mu m$ surface scans of PSZT thin films deposited at sputtering pressures of (a) 10 mTorr and (b) 30 mTorr.
2.2.4 Section conclusions

This sub-section summarises the results obtained from the analyses of PSZT thin films deposited under different sputtering pressures. The composition, orientation, and surface roughness of thin films sputtered at oxygen partial pressures of 1, 2, 3, 4, and 5 mTorr have been characterised and compared. XPS and GA-XRD results complement each other, with observable effects due to either excess lead or oxygen. Increasing the sputtering pressure increased lead concentration due to diffusion-based transport of species (and this can be used to prevent lead loss in deposited films). High levels of lead resulted in an increase in the exhibited \(d\)-spacings and high levels of oxygen resulted in a decrease in \(d\)-spacing, from expected values. Surface morphology studies do not indicate an identifiable trend, but highlights the presence of agglomerates in some cases. The PSZT thin films deposited at a sputtering pressure of 10 mTorr (oxygen partial pressure 1 mTorr) have given the best results – desired composition (close to the desired \(ABO_3\)) and orientation, with low surface roughness and uniformly sized grains. These results are also presented in [2.7].

2.3 Identification of Modified PSZT Unit Cell

Having identified suitable deposition conditions in terms of post-deposition cooling rate and sputtering pressure, the choice of temperature of deposition of the PSZT thin films was addressed. Substrate temperatures of 500 to 700 °C are normally used for the deposition of thin films of PZT compounds, to attain desired perovskite structure [2.1, 2.8]. In order to incorporate these piezoelectric thin films into standard devices, deposition on silicon substrates is desirable. Deposition of PZT has been conventionally carried out on platinum-coated silicon substrates [2.1, 2.8]. Considering the inert properties of gold and that its lattice spacings are close to those of PSZT [2.9], deposition on gold-coated silicon substrates was also investigated. As the gold-silicon
eutectic point is 363 °C, deposition on gold coated substrates was limited to 300 °C. Considering these preliminary choices, deposition at 300 °C on gold and at 600-700 °C on platinum was investigated.

This sub-section reports on the influence of multi-layered bottom electrodes (with gold or platinum) on the orientation of deposited PSZT thin films of the composition (Pb_{0.92}Sr_{0.08})(Zr_{0.65}Ti_{0.35})O_{3}. For this composition, the films are expected to have a rhombohedral unit cell at room temperature (corresponding to space group R3c) \cite{2.10}; and so, the corresponding powder diffraction file was used as a reference \cite{2.11}. Bragg-Brentano X-ray diffraction (XRD) was used to experimentally determine the d-spacings in the deposited PSZT thin films, in order to calculate the unit cell parameters. These results have been used to index X-ray diffractograms for PSZT thin films deposited on different multi-layer bottom electrode configurations, and to identify those that promote perovskite orientation.

The XRD analysis carried out showed that a majority of the PSZT peaks were shifted from the expected 2θ positions \cite{2.11}; X-ray photoelectron spectroscopy was used to confirm that composition of the films was very close to that of the reference used \cite{2.7, 2.11}. As the diffractometer was regularly calibrated using a quartz standard, errors introduced by the system were ruled out. The as-deposited metal films (gold and platinum) at room temperature were expected to be nanocrystalline; but the temperatures at which PSZT deposition was carried out resulted in grain growth with preferential orientation, manifested as strong (111) metal peaks. These (111) metal peaks were at the expected 2θ positions \cite{2.9, 2.12}, again verifying that the PSZT peaks were shifted from the expected. From these results, unit cell parameters for PSZT deposited on gold and platinum were calculated, which indicated that two modified unit cells existed based on deposition temperature and substrate.
2.3.1 Modified PSZT unit cell on gold at 300 °C

Using $d$-spacings obtained from XRD (for the $2\theta$ range of 20°-60°) the unit cell parameters for the PSZT thin films deposited on gold were estimated. The results obtained are summarised in Table 2.4.

**Table 2.4:** Comparison between expected, experimental, and equivalent lattice spacings for PSZT on gold.

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Expected $d$-spacings based on ICDD PDF 04-002-5985 Å</th>
<th>Experimental $d$-spacing values from XRD Å</th>
<th>Equivalent $d$-spacings calculated from experimentally derived unit cell Å</th>
<th>Difference in equivalent $d$-spacings from expected values %</th>
</tr>
</thead>
<tbody>
<tr>
<td>(012)</td>
<td>4.0793</td>
<td>-</td>
<td>4.295</td>
<td>+5.288</td>
</tr>
<tr>
<td>(004)</td>
<td>-</td>
<td>3.767</td>
<td>3.769</td>
<td>-</td>
</tr>
<tr>
<td>(104)</td>
<td>2.9033</td>
<td>3.058</td>
<td>3.057</td>
<td>+5.294</td>
</tr>
<tr>
<td>(110)</td>
<td>2.8661</td>
<td>-</td>
<td>3.018</td>
<td>+6.661</td>
</tr>
<tr>
<td>(113)</td>
<td>2.4570</td>
<td>2.623</td>
<td>2.587</td>
<td>+5.291</td>
</tr>
<tr>
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<td>2.3862</td>
<td>2.503</td>
<td>2.513</td>
<td>+5.314</td>
</tr>
<tr>
<td>(202)</td>
<td>2.3451</td>
<td>-</td>
<td>2.469</td>
<td>+5.283</td>
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<tr>
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</tr>
<tr>
<td>(211)</td>
<td>1.8604</td>
<td>-</td>
<td>1.959</td>
<td>+5.300</td>
</tr>
<tr>
<td>(116)</td>
<td>1.8338</td>
<td>1.932</td>
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<tr>
<td>(214)</td>
<td>1.6618</td>
<td>-</td>
<td>1.750</td>
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<tr>
<td>(300)</td>
<td>1.6547</td>
<td>-</td>
<td>1.742</td>
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<tr>
<td>(125)</td>
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<td>+5.263</td>
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<tr>
<td>(034)</td>
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</tr>
<tr>
<td>(028)</td>
<td>-</td>
<td>1.531</td>
<td>1.528</td>
<td>-</td>
</tr>
</tbody>
</table>

These results show that the majority of the equivalent (i.e. calculated) $d$-spacings show an increase of about 5.26-5.31%. The resulting change in both the rhombohedral
unit cell parameters $a$ and $c$ is +5.29 %; from the expected $a$ of 5.732 Å and $c$ of 14.317 Å to 6.035±0.010 Å and 15.075±0.015 Å, respectively. This corresponds to an increase in the unit cell volume by about 16 %.

2.3.2 Modified PSZT unit cell on platinum at 650 ºC

Table 2.5: Comparison between expected, experimental, and equivalent lattice spacings for PSZT on platinum.

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Expected d-spacings based on ICDD PDF 04-002-5985 Å</th>
<th>Experimental d-spacing values from XRD Å</th>
<th>Equivalent d-spacings calculated from experimentally derived unit cell Å</th>
<th>Difference in equivalent d-spacings from expected values %</th>
</tr>
</thead>
<tbody>
<tr>
<td>(012)</td>
<td>4.0793</td>
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<td>4.043</td>
<td>-0.890</td>
</tr>
<tr>
<td>(104)</td>
<td>2.9033</td>
<td>3.014</td>
<td>3.015</td>
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</tr>
<tr>
<td>(110)</td>
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<tr>
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<td>2.4570</td>
<td>-</td>
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<td>(006)</td>
<td>2.3862</td>
<td>2.614</td>
<td>2.613</td>
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<td>2.3451</td>
<td>2.106</td>
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<td>2.027</td>
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<tr>
<td>(211)</td>
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<td>-</td>
<td>1.772</td>
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</tr>
<tr>
<td>(116)</td>
<td>1.8338</td>
<td>1.956</td>
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<tr>
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<td>1.8150</td>
<td>-</td>
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</tr>
<tr>
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<td>1.6836</td>
<td>1.849</td>
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<td>1.6618</td>
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<td>-2.275</td>
</tr>
<tr>
<td>(300)</td>
<td>1.6547</td>
<td>1.577</td>
<td>1.573</td>
<td>-4.937</td>
</tr>
<tr>
<td>(125)</td>
<td>1.5694</td>
<td>-</td>
<td>1.550</td>
<td>-1.236</td>
</tr>
<tr>
<td>(028)</td>
<td>-</td>
<td>1.510</td>
<td>1.508</td>
<td>-</td>
</tr>
</tbody>
</table>

In a similar manner to the above, the unit cell parameters for the PSZT thin films deposited on platinum were estimated. The results obtained are summarised in Table 2.5. These results show the equivalent $d$-spacings increase or decrease based on the
dominating unit cell parameters for the chosen orientation. The resulting changes in the rhombohedral unit cell parameters $a$ and $c$ were $-4.92\%$ and $+9.49\%$, respectively; this change is from the expected $a$ of 5.732 Å and $c$ of 14.317 Å to $5.450\pm0.010\,\text{Å}$ and $15.675\pm0.015\,\text{Å}$, respectively. This corresponds to a decrease in the unit cell volume by about $1\%$.

### 2.3.3 Orientation of PSZT thin films on gold at 300 °C

PSZT thin films were deposited on silicon samples coated with 150 nm of gold with a 15 nm titanium adhesion layer. Figure 2.4(a) shows the resulting diffractogram for such films; here two perovskite PSZT peaks can be observed. Cross-sectional transmission electron microscopy (JEOL 2010F TEM) of these samples indicated that interdiffusion had occurred between the bottom electrode layers and silicon (Section 3.2 and in [2.13]). This could be attributed to the fact that the PSZT deposition on these samples was carried out at 300 °C, which is close to the eutectic point of gold and silicon – the eutectic point could have been reached as the vapour pressure at the sputtering pressure would have been lower.

In order to overcome this undesirable reaction, a 200 nm silicon dioxide layer was introduced to isolate the metals from silicon. This increased the preferential (111) orientation, relative to the (200) peak, of the underlying gold layer [2.9] and also the relative intensity of the perovskite (104) PSZT orientation as shown in Fig. 2.4(b). Cross-sectional transmission electron microscopy studies have confirmed that this added silicon dioxide layer prevents the reaction between gold and silicon (Section 3.3). Deposition duration did not influence the orientation of the PSZT thin films, with the ratio of relative intensities of the preferential orientations remaining unaffected. However, the extent of preferential orientation in the underlying gold layer increased, due to continued grain growth.
Figure 2.4: X-ray diffractograms obtained for PSZT thin films deposited on silicon samples coated with 150 nm Au using a 15 nm Ti adhesion layer without and with an intermediate 200 nm SiO₂ layer are shown in (a) and (b), respectively.
2.3.4 Orientation of PSZT thin films on platinum at 650 ºC

PSZT thin films were deposited on a number of platinum-based bottom electrode configurations on silicon substrates, as listed below:

(i) 200 nm Pt / 20 nm Ti / Si
(ii) 200 nm Pt / 20 nm Ti / 200 nm SiO₂ / Si
(iii) 300 nm Pt / 70 nm Ti / 200 nm SiO₂ / Si
(iv) 200 nm Pt / 20 nm TiO₂ / Si

PSZT thin films on platinum require heating to temperatures of 600 ºC and above to enhance the perovskite structure; hence, all depositions of PSZT on platinum were carried out at 650 ºC [2.1, 2.8]. Films deposited on electrode configuration (i) were found to have high surface roughness due to the formation of platinum-titanium silicide at these temperatures (verified by Auger electron spectroscopy), but perovskite PSZT peaks were observed [Fig. 2.5(a)]. A silicon dioxide layer was introduced to inhibit this silicide formation [configurations (ii) and (iii)], along with experimenting with thicker platinum and titanium layers [configuration (iii)], in order to preserve the smooth platinum surface. PSZT thin films deposited on electrode configurations (ii) and (iii) were not usable, as the underlying layers delaminated due to stress imbalance between the various layers. This is attributed to the differences in coefficients of thermal expansion and ratio of thicknesses of the different layers [2.14]. Titanium dioxide layers (known to be stable and inert) were experimented with, and PSZT thin films deposited on electrode configuration (iv) were very smooth, as the reaction between platinum and titanium was prevented, and preferential perovskite PSZT orientation was obtained [Fig. 2.5(b)].
Deposition of PSZT thin films on platinum was also carried out at 600 °C and 700 °C, and there were no significant differences in the preferential orientations with temperature. Deposition durations of two and four hours also resulted in almost identical diffractograms, with just the substrate peaks suppressed for samples from longer depositions.
2.3.5 Section conclusions

This sub-section discusses the orientation dependence of PSZT thin films on bottom electrode architectures. XRD results highlighted variations in obtained 2θ peak positions from expected positions, indicating the existence of modified unit cells for PSZT thin films on gold and platinum. The modified rhombohedral unit cell parameters and the equivalent d-spacings are discussed. The variations in unit cell parameters from expected values could be attributed to guiding effects from the crystalline bottom electrode layers; and variations appear consistent with the larger lattice spacings for gold in comparison to platinum. Considering the second variable of deposition temperature, additional work on other substrates (Appendix B) indicates that the deposition temperature influences the unit cell structure the most. The structure obtained on gold-coated silicon at 300 ºC is unique to such gold-coated substrates, apparently due to the guiding effect exhibited by (111) gold on (104) PSZT (discussed in Sections 3.3 and 5.1). No preferential orientation was observed on other materials (such as LiNbO₃, Pt, etc.) at 300 ºC.

2.4 Conclusions

This chapter presented the investigations carried out in identifying optimal deposition conditions for PSZT thin films. The influence of oxygen partial pressure, bottom metal electrode choice, and substrate temperature on the composition and crystal structure of the resulting thin films was analysed. The potential variables identified in Table 2.1 have now been replaced with optimised parameters (Table 2.6).
Table 2.6: Optimised PSZT thin film deposition conditions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target</td>
<td>(Pb$<em>{0.92}$Sr$</em>{0.08}$)(Zr$<em>{0.65}$Ti$</em>{0.35}$)O$_3$</td>
</tr>
<tr>
<td>Target diameter</td>
<td>100 mm</td>
</tr>
<tr>
<td>RF power</td>
<td>100 W</td>
</tr>
<tr>
<td>Target to substrate distance</td>
<td>70 mm</td>
</tr>
<tr>
<td>Base pressure</td>
<td>9.0 x 10$^{-6}$ Torr</td>
</tr>
<tr>
<td>Sputtering pressure</td>
<td>1.0 x 10$^{-2}$ Torr</td>
</tr>
<tr>
<td>Process gas</td>
<td>10% oxygen in argon</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>300 °C$^a$ or 600-700 °C$^b$</td>
</tr>
<tr>
<td>Temperature ramp-up rate</td>
<td>10 °C/min</td>
</tr>
<tr>
<td>Temperature ramp-down rate</td>
<td>5 °C/min</td>
</tr>
</tbody>
</table>

$^a$ Suitable for deposition on gold  
$^b$ Suitable for deposition on platinum

During the course of identification of optimal deposition conditions, the following key results have been obtained:

A. Conditions to achieve desired PSZT thin film composition have been identified.

B. In studying the influence of oxygen partial pressure on thin film composition, conditions for deposition of controlled lead-rich films have been identified. This will serve as a technique to design film composition in order to overcome lead loss due to subsequent processing.

C. Suitable bottom electrode architectures for device designs and piezoelectric response measurements have been identified.

D. Two different modified unit cell structures of PSZT, based on the guiding effect of gold (at 300 °C) or as a consequence of temperature (at 650 °C), have been identified. This result demonstrates an approach for tailoring the crystal structure of the material.
CHAPTER 3

MATERIALS CHARACTERISATION OF PSZT THIN FILMS

3.1 Introduction

PSZT thin films deposited by RF magnetron sputtering were analysed in detail using a combination of spectroscopy, microscopy, and diffraction techniques. This chapter presents the results from these analyses and discusses the scientific outcomes attained. The experimental details for these techniques are described in Appendix A. PSZT thin films were deposited on gold (Au) and platinum (Pt) coated silicon substrates, and two different combinations of adhesion layers were used for each metal. The resulting four categories of multi-layer thin film structures as shown below were analysed:

(i) PSZT / 150 nm Au / 15 nm Ti / Si → PSZT on Au/Ti/Si
(ii) PSZT / 150 nm Au / 15 nm Ti / 200 nm SiO₂ / Si → PSZT on Au/Ti/SiO₂/Si
(iii) PSZT / 200 nm Pt / 20 nm TiO₂ / Si → PSZT on Pt/TiO₂/Si
(iv) PSZT / 200 nm Pt / 20 nm Ti / Si → PSZT on Pt/Ti/Si
### 3.2 PSZT Thin Films on Au/Ti/Si

Having chosen gold for having lattice spacings close to those of PSZT, thin films deposited on gold coated silicon substrates, with a titanium adhesion layer, were characterised. XRD results for these samples are discussed in Section 2.3.3 [Fig. 2.4(a)], where it is shown that these films were preferentially oriented.

#### 3.2.1 Composition analysis

X-ray photoelectron spectroscopy (XPS) was used to verify that thin films deposited were of the desired composition. The films were found to have a chemical composition close to that of the sputtering target under the deposition conditions chosen (Section 2.2.1). As XPS analyses the film only to the depth of a few nanometers, secondary ion mass spectrometry (SIMS) depth profiling was performed.

![Secondary ion mass spectroscopy depth profile of a PSZT thin film deposited on Au/Ti/Si.](image)

**Figure 3.1:** Secondary ion mass spectroscopy depth profile of a PSZT thin film deposited on Au/Ti/Si.
Secondary ion mass spectrometry depth profiling through the film thickness (Fig. 3.1) showed that it was compositionally uniform. The SIMS data also highlighted some dissolution of the titanium into the gold layer, although the peak in the titanium signal corresponded to the location of the original titanium layer (between the gold layer and the silicon substrate). This depth profile was used to explain the results of certain observations during the transmission electron microscopy analysis (discussed in Section 3.2.4).

### 3.2.2 Surface morphology analysis

AFM scans of PSZT thin films deposited at 300 °C on gold were analysed to study surface variations with respect to sputtering duration (Fig. 3.2). The average surface roughness of films deposited for 1, 2, and 4 hours were 5.5 nm, 7.8 nm, and 9.5 nm, respectively. This indicates a rougher film surface for increased deposition duration, which is due to increasing grain sizes of the films; this can be clearly observed in Fig. 3.2.
3.2.3 Intrinsic multi-layer stress analysis

An Ambios Instruments XP-2 surface/stylus profilometer was used for stress measurements. The profilometer was used to measure the radius of curvature induced in substrates by the deposited thin films. This curvature can be related to stress using Stoney’s equation [3.1]. The resulting level of stress in the multi-layer structure was estimated.
\[ \sigma = \frac{1}{6R} \frac{E}{1-\nu} \frac{t_s^2}{t_f} \]

where  
- \( R \) = radius of curvature  
- \( E / (1-\nu) \) = substrate elastic constant  
- \( E \) = Young's Modulus  
- \( \nu \) = Poisson's Ratio  
- \( t_s \) = substrate thickness  
- \( t_f \) = film thickness

The profilometer software was used to perform these calculations based on a least squares fit method [3.1], using parameters for (100) silicon substrates. The scans performed were over 5 mm centred on the sample at a scan speed of 0.1 mm/s, with a stylus force of 0.05 mg. All stress values indicated for samples are the average of two perpendicular scans. Compressive stress has been indicated using negative values and tensile stress using positive values.

Figure 3.3: Results of stress measurements for PSZT thin films deposited on Au/Ti/Si at 300 ºC for 1 hour (~400 nm thick) and 2 hours (~800 nm thick).

The thin film structures on gold were found to exhibit compressive stress. The variation in stress with PSZT deposition duration has been determined. A deposition duration of 1 hour results in PSZT films which are about 400 nm thick, while a
deposition duration of 2 hours results in a thickness of about 800 nm. It can be observed in Fig. 3.3 that increasing deposition duration results in reduced stress, with an appreciable drop in stress levels by an order of magnitude.

3.2.4 Transmission electron microscopy analysis

Figure 3.4: XTEM analyses of a PSZT thin film deposited for a sputtering duration of 2 hours are shown. (a) Bright field image of the ~470 nm thick PSZT film on a ~130 nm thick gold layer. Prismatic ingrowths projecting into the silicon substrate can be observed. (b) Hollow cone dark field image of the PSZT film highlighting the columnar structure. Note: The outer region (~100 nm) of the film in (b) has been removed during ion-milling.

Figure 3.4(a) shows a low magnification cross-sectional view of the multi-layer structure. Energy dispersive X-ray analysis (EDX) was carried out along the length and through the thickness of the film to detect gross variations in chemical composition due to second phases or other contaminants; none were found. The PSZT film was uniform in thickness (~470 nm). The dark band beneath the film is the gold-titanium-silicon layer (typically ~135 nm thick), from which prismatic ingrowths into the silicon substrate can be seen. SIMS depth profiling through the film thickness (Section 3.2.1, Fig. 3.1)
showed that it was compositionally uniform (also shown in Fig. 3.5). The SIMS data also highlighted some dissolution of the titanium into the gold layer.

Figure 3.5: Secondary ion mass spectroscopy depth profile of a PSZT thin film deposited on Au/Ti/Si. (Same as Fig. 3.1)

Figure 3.6: High resolution cross-sectional TEM image of the amorphous layer at the interface of PSZT and gold.
Detailed imaging of this interfacial region (Fig. 3.6) showed an amorphous layer approximately 4 nm thick. Point analysis with EDX showed that this layer was rich in silicon and oxygen, most likely SiO$_2$ formed by outward diffusion of silicon from the substrate through the metal layers. This is supported by previous studies on the fast outward diffusion of silicon through grain boundaries in gold [3.2], with this silicon oxidising in the 10 % oxygen in argon sputtering atmosphere. This is also supported by the increase in the silicon signal at this interface in the SIMS analysis (also confirming that this is not a by-product of the specimen preparation ion milling process). The region of PSZT (~25 nm) closest to this amorphous layer appeared to be amorphous or at best poorly crystalline, as it exhibited strong amorphous speckle (right inset of Fig. 3.6). Weak lattice fringe contrast was evident only from regions greater than 30 nm into the PSZT layer (from the amorphous interfacial layer, as seen in the left inset of Fig. 3.6).

The PSZT thin film exhibited a columnar microstructure (Fig. 3.4). These columnar grains were perpendicular to the substrate (out of plane), and were most apparent in the energy filtered (zero loss) hollow cone dark field (HCDF) image [of a 2 hour PSZT deposition sample shown in Fig. 3.4(b)]. Typical columnar grain widths were 30-50 nm, and many grains appeared to span the full thickness of the film (~470 nm). The contrast due to the crystallinity was quite weak in the 25 nm thick band of PSZT closest to the gold layer, confirming the amorphous or poorly crystalline nature of this region (as observed in Fig. 3.6). During the initial stages of deposition, the PSZT was deposited onto a substrate covered with amorphous SiO$_2$, which affected crystallinity. Crystallisation of the PSZT occurs once a certain thickness of material (~25 nm) has been deposited. Growth stress may contribute to the onset of crystallisation [3.3]. X-ray diffraction analysis of these films showed that the films exhibited preferential [104] orientation [Section 2.3.3, Fig. 2.4(a)].
Increasing the deposition duration from 2 to 4 hours increased the columnar grain width (measured from hollow cone dark field images) from 30-50 nm to ~90 nm. It also resulted in an increase in the average surface roughness ($R_a$) from 7.8 nm to 9.5 nm [3.4, 3.5]. This was attributed to the development of marked faceting. Fig. 3.4(a) shows a cross-section of the relatively flat surface of the film deposited for 2 hours. The dimension of the weak faceting is similar to that of the columnar grain width (30-50 nm). For the film deposited for 4 hours, very pronounced prismatic faceting has occurred (Fig. 3.7). This is much coarser than seen at the shorter duration and reflects the grain coarsening taking place in the film in longer duration depositions. The increase in roughness is a consequence of grain coarsening, which can be attributed to the variations in growth rates as a function of crystal orientation as well as grain coalescence. At the growing surface, those grains in orientations promoting faster growth can dominate neighbouring grains and eventually isolate them. With continued growth, grains may then develop prismatic faceting which causes increased surface roughening as the grain width increases [3.3].

![Figure 3.7: Cross-section TEM image showing the highly faceted film surface with crystallites at the gold-silicon interface.](image)

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The eutectic point of gold and silicon is 363 °C, but at the deposition temperature of 300 °C interdiffusion of gold and silicon (enabled by outward silicon diffusion through gold grain boundaries) through the 15 nm thin titanium adhesion layer has been observed. This reaction was verified using secondary ion mass spectroscopy (SIMS) depth profiling (Fig. 3.5). The peak titanium concentration occurred between gold and silicon – being the original location of the ~15 nm thick titanium layer. On moving through the gold layer towards the PSZT (a distance of 150 nm), the titanium signal showed a gradual decrease. This indicated that interdiffusion of gold and titanium had occurred. Both titanium and gold diffusion into silicon was also apparent. The profiles for these two elements were very similar and gradually decreased over a considerable distance into the silicon. Due to the very different sputtering rates of the various phases present, it was not possible to meaningfully estimate the depth over which the gold and titanium diffused into the silicon substrate. However, the cross-sectional TEM imaging provided an understanding of the origin of the SIMS profile shapes for these elements.

Figure 3.8: Cross-sectional TEM image of a crystallite bounded by dense (111) silicon planes. The angle between the silicon (100) surface and the crystallite edge is 54.7° being the silicon (100)\textsuperscript{\texttt{*}}(111) interplanar angle. Note: The electron beam is parallel to silicon [110].
The gold-(titanium)-silicon reaction can be observed in the form of prismatic crystallites growing into silicon along the metal-silicon interface. This is shown in Figs. 3.4 and 3.7 and in detail in Fig. 3.8. EDX analysis confirmed that these crystallites were a reaction product of gold and silicon – with titanium also present. The remnant of the original titanium layer could be seen as a ~8 nm wide band running across the base of the crystallite in Fig. 3.8. The crystallites were variable in size, the largest being about 200 nm into silicon. During SIMS depth profiling (Fig. 3.5), the floor of the ion milling crater would break through the main (flat) part of the metal layer into the silicon substrate, and the gold and titanium signals would be expected to drop abruptly. However, the presence of prismatic crystallites rich in gold, with traces of titanium, projecting into the silicon substrate, would cause the signal for these elements to taper off gradually as the depth profiling progressed, dropping to zero when the profile passed through the apex of the largest crystallites.

The diffusion of gold into the (100) silicon results in crystallites bounded by the dense (111) silicon planes (Fig. 3.8). As expected the angle between these bounding planes and the silicon (100) surface was found to be 54.7º in Fig. 3.8, which is oriented with the electron beam parallel to silicon [110]. The resulting gold crystallites varied in size and the density of such crystallites was much higher in longer duration deposition (4 h) specimen. Such diffusion or dissolution of gold into silicon-based materials through titanium has been observed [3.6] and can be related to the high reactivity of titanium with silicon (Ti$_x$Si$_y$ compounds are formed even at slightly elevated temperatures) and the limited thickness (15 nm) of the titanium layer. Kanamori and Sudo [3.7] have reported that the titanium layer needs to have a sufficient thickness, depending on process temperature and duration, in order to serve as a barrier to prevent the gold-silicon reaction, rather than serve only as an adhesion layer (in these
3.2.5 *Section conclusions*

Analysis of the chemical composition of the PSZT thin films indicated that composition close to that of the sputtering target was obtained. SIMS depth profiling highlighted the presence of interdiffusion of metals and silicon, which was analysed further using transmission electron microscopy.

For the PSZT thin films deposited on Au/Ti/Si, trends observed from the surface morphology and stress analyses are: (i) an increase in the size of grains with deposition duration, (ii) an increase in the average surface roughness with deposition duration, and (iii) a decrease in the level of compressive stress with deposition duration.

Transmission electron microscopy (TEM)-based characterisation of strontium-doped lead zirconate titanate (PSZT) thin films deposited on Au/Ti/Si was carried out. The PSZT thin films had a columnar grain structure. A silicon-rich amorphous layer was formed at the interface of the PSZT thin films and gold, and is most likely silicon dioxide. Prismatic crystallites of a gold-silicon compound developed at the interface of the metal layers and the silicon substrate. This was caused by gold diffusing through the underlying titanium metal layer; the crystallites being bounded by the dense (111) silicon planes.

3.3 **PSZT Thin Films on Au/Ti/SiO$_2$/Si**

To prevent the gold-silicon reaction observed in the case of PSZT thin films on Au/Ti/Si by fast outward diffusion of silicon, an intermediate silicon dioxide (SiO$_2$, 200
nm thick) layer was introduced between the metal layers and silicon. Considering results from the analysis of PSZT thin films on Au/Ti/Si, it was apparent that transmission electron microscopy served as the most valuable tool in identifying interdiffusion and the presence of any amorphous or poorly crystalline region. Therefore, after verifying the composition of these thin films using XPS, efforts were focussed on transmission electron microscopy analysis of these samples.

### 3.3.1 Transmission electron microscopy analysis

The PSZT thin films deposited on Au/Ti/SiO₂/Si had an average surface roughness ($R_a$) of 16-20 nm with grains 30-60 nm in width. The PSZT deposition temperature (300 °C) initiates crystal growth in the gold layer (which was nanocrystalline when deposited), resulting in significant changes to the texture of gold (Fig. 3.9).

![Figure 3.9: Cross-sectional TEM analysis of PSZT thin films on Au/Ti/SiO₂/Si. (a) The silicon dioxide layer included between the metal layers and the silicon substrate prevents metal-silicon reactions, and uniform thin film layers can be observed in the cross-sectional transmission electron micrograph. Columnar grain growth in the PSZT thin film can be observed. (b) The deposition temperature causes grain growth in the gold layer, resulting in large crystalline grains and voids at the grain boundaries. This results in the gold layer having a preferential (111) orientation (lattice spacing of 0.236 nm).](image)
The ratio of the relative intensities of the (111) and (200) gold X-ray diffraction peaks was ~100 after PSZT deposition at 300 °C on a sample with the buffer layer of silicon dioxide [Section 2.3.3, Fig. 2.4(b)]; this corresponds to an increase in preferential orientation in the gold layer by a factor of 6 (compared to a sample without the silicon dioxide layer) [3.8]. In the absence of gold-silicon interactions, the gold crystallites are able to reorient so that the most densely packed planes (111) are parallel to the surface, and thus the surface energy is minimised. The formation of the amorphous layer is also prevented. As a result, the highly textured gold layer was able to exert a strong guiding effect on the subsequently deposited PSZT thin films (Fig. 3.10), which developed pronounced (104) texture. This guiding effect can be observed in the micrograph in Fig. 3.10, where (104) PSZT planes are aligned parallel to (111) gold planes; this is a feature at different points along the interface interspersed with regions of random orientation.

**Figure 3.10:** Cross-sectional transmission electron micrographs showing the guiding effect of gold. The lattice spacing of 0.236 nm corresponds to interplanar (111) Au spacings and 0.305 nm to (104) PSZT spacings.
The pronounced (111) orientation in the gold layer improves the preferential orientation of the PSZT thin film – the ratio of the X-ray diffraction relative intensities of the two major peaks corresponding to (004) and (104) PSZT orientations increased from 1.57 to 8.52 with the inclusion of the silicon dioxide layer (Section 2.3.3 and [3.8]). The PSZT thin film also has a strong columnar grain structure, evident in Fig. 3.9(a).

### 3.3.2 Crystal structure simulations

Crystal structure simulations were carried out to verify the possibility of the guiding effect observed. These simulations were performed using the modified unit cell parameters for PSZT (Section 2.3.3 and [3.8]) and the standard gold structure [3.9].

![Crystal structure simulation](image)

**Figure 3.11:** Crystal structure simulation showing the superposition of the gold (111) plane on the PSZT (104) plane. From the overlap of atoms of these planes it can be concluded that gold can exert a guiding effect on PSZT. The simulation for gold was based on a lattice constant \(a\) of 0.236 nm and that for PSZT was based on the modified rhombohedral unit cell parameters \(a\) of 0.604 nm and \(c\) of 1.508 nm (as described in Section 2.3.1).
Figure 3.11 shows the results of the simulations, and overlap of atoms of the (104) PSZT plane with those of the (111) gold plane is apparent. This validated the choice of gold as a bottom electrode layer, defying convention. The choice was made due to the lattice spacings of gold being similar to those of PSZT, and this choice directly resulted in the guiding effect and resulting preferential orientation observed.

### 3.3.3 Section conclusions

This section clearly shows the marked improvement in microstructure of the PSZT thin film as a direct result of the inclusion of the 200 nm silicon dioxide layer. The silicon dioxide layer served as a barrier for intermetallic diffusion and enabled strong preferential orientation in gold, driven by thermally activated grain growth. The (111) oriented gold layer had a guiding effect on the subsequently deposited PSZT, resulting in a strong (104) preferential orientation in the thin films. This microstructural analysis explains the improved preferential orientation observed in the X-ray diffraction analysis of Section 2.3.3.

### 3.4 PSZT Thin Films on Pt/TiO₂/Si

As platinum has been the conventional choice for deposition of PZT compounds, microstructural analysis of samples of PSZT thin films deposited on platinum-coated silicon substrates was carried out. These substrates utilised a 20 nm thick titanium dioxide (TiO₂) layer to promote adhesion of platinum to silicon, and titanium dioxide was chosen due to its inert nature.

As these samples were deposited during the initial stages of this doctoral program, analyses similar to those for PSZT/Au/Ti/Si (Section 3.2) were carried out. XRD results for these samples showed that these films were preferentially oriented,
with a strong (104) orientation, as discussed in Section 2.3.4 [Fig. 2.5(b)].

3.4.1 Composition analysis

X-ray photoelectron spectroscopy (XPS) was used to verify that the PSZT thin films had a chemical composition close to that of the target under the deposition conditions chosen (Section 2.2.1). In addition, secondary ion mass spectrometry (SIMS) depth profile analysis was carried out.

![SIMS depth profile](image)

**Figure 3.12:** Secondary ion mass spectroscopy depth profile of a PSZT thin film deposited on Pt/TiO$_2$/Si.

The SIMS depth profile (Fig. 3.12) indicated that the films were of extremely uniform composition through their thickness. Moreover, no undesirable intermixing between the multilayer electrode and silicon was observed.
3.4.2 Surface morphology analysis

Figure 3.13: Atomic force microscope scans over an area of 1 μm × 1 μm of PSZT thin films deposited on Pt/TiO₂/Si for 2 hours at (a) 600 ºC, (b) 650 ºC, and (c) 700 ºC.
AFM surface scans of PSZT thin films deposited for 2 hours on platinum were analysed to study surface variations with respect to the deposition temperature (Fig. 3.13). The average surface roughness of films deposited at 600 °C, 650 °C, and 700 °C were 5.2 nm, 5.0 nm, and 4.7 nm, respectively. Temperature appears to have very little influence on the average surface roughness of thin films deposited on platinum, but appears to have a more obvious influence on the thin film orientation [3.10] and on the nature and arrangement of grains as can be observed in Fig. 3.13.

3.4.3 Intrinsic multi-layer stress analysis

Most PSZT thin films deposited on platinum exhibited tensile stress. The variations in stress with the deposition substrate temperature and with the deposition duration have been determined. The study with respect to deposition substrate temperature was carried out for 2 hour depositions (approximately 800 nm thick films) at temperatures of 600 °C, 650 °C, and 700 °C. Stress analysis of thin films deposited at 700 °C for 1 and 2 hours was also performed.

Figure 3.14(a) demonstrates the observed trend of increasing stress with deposition temperature. Figure 3.14(b) shows the decreasing stress with increasing deposition duration, and the change in nature of stress from tensile to compressive. This observation is similar to the phenomenon observed for PSZT thin films on gold (Fig. 3.3).

Figure 3.15 shows the trend observed when results for deposition at 300 °C on gold and at 600 °C, 650 °C, and 700 °C on platinum are combined. These trends indicate that low temperature depositions combined with thicker films result in the least stress.
Figure 3.14: Results of stress measurements for PSZT thin films deposited on platinum for (a) 2 hours at 600 ºC, 650 ºC, and 700 ºC and (b) for 2 hours and 4 hours at 700 ºC.

Figure 3.15: Observed trend in measured stress for PSZT thin films with increasing deposition temperature.
3.4.4 Transmission electron microscopy analysis

Cross-sectional transmission electron microscopy analysis of PSZT thin film samples revealed the existence of a highly ordered columnar grain structure, as shown in Fig. 3.16(a). Hollow cone illumination revealed that a large number of grains share the similar orientation [Fig. 3.16(b)].

![Cross-sectional energy filtered TEM images](image)

**Figure 3.16:** Cross-sectional energy filtered TEM images: (a) bright field diffraction contrast image of the columnar grain structure in the PSZT thin films deposited on platinum and (b) hollow cone dark field image illuminating grains with similar orientation.

The temperature of PSZT deposition results in grain growth in the platinum bottom electrode layer (deposited at room temperature), resulting in preferential (111) orientation of platinum (verified by X-ray diffraction). This grain growth also resulted in voids in the platinum thin film.

The densely-packed and ordered columnar structure of the PSZT thin film was apparent in atomic force microscopy scan results (Fig. 3.13) and was also observed using high resolution field emission gun scanning electron microscopy (Fig. 3.17).
Figure 3.17: Field emission gun scanning electron micrograph of the PSZT thin film surface. (Sample tilt 70º)

3.4.5 Section conclusions

This section shows that the PSZT thin films deposited on Pt/TiO₂/Si were of uniform composition. The following trends were observed from the stress analysis and surface morphology results: (i) very little dependence of the average surface roughness on deposition temperature, (ii) a notable influence of deposition temperature on the structure, orientation, and nature of grains, (iii) an increase in the levels of tensile stress in the thin films with increasing deposition temperature, and (iv) a decrease in stress of thin films deposited at 700 °C with increasing duration. Electron microscopy analysis results confirmed that these films had a very regular and columnar microstructure, which can be related to strong preferential c-axis orientation as observed in corresponding X-ray diffractograms [Fig. 2.5(b)].
3.5 PSZT Thin Films on Pt/Ti/Si

PSZT thin films deposited on Pt/Ti/Si were initially analysed by X-ray diffraction [Section 2.3.4 and Fig. 2.4(a)], and peaks corresponding to reaction between platinum and silicon were observed. This undesirable reaction between platinum and silicon, resulted in a rough PSZT thin film surface. Though this reaction was construed undesirable, potential applications of this reaction for self-assembly driven deposition of PSZT (discussed in Section 5.2) initiated investigation of this category of films, which were analysed using transmission electron microscopy.

3.5.1 Transmission electron microscopy analysis

The temperature of deposition initiates a reaction between platinum and silicon through the thin titanium layer, resulting in the formation of islands of platinum silicide. The deposited PSZT thin film layer grows preferentially on these platinum silicide islands. The platinum-silicon reaction and growth of nanoscale PSZT islands, with columnar grains, can be seen in Fig. 3.18. These films exhibit weaker preferential orientation, compared to their continuous counterparts. The mechanism of formation of these platinum-silicon island structures is described in the next sub-section (Section 3.5.2).
3.5.2 Mechanism of Pt-Si island formation

The mechanism of formation of the platinum-silicon islands was investigated using *in situ* heating during plan view transmission electron microscopy analysis. Silicon substrates coated with 200 nm of platinum with a 20 nm titanium adhesion layer...
were used. These samples were mechanically polished to create plan view TEM specimens. A TEM holder with a programmable heating element, and temperature accuracy of ±0.5 °C, was used. The heating cycle was designed to replicate the temperature ramp-up before the PSZT sputtering process.

Figure 3.19: Evolution of grains in the Pt/Ti/Si structure: (a) as-deposited sample, (b) at 500 °C, and (c) at 650 °C.
Observing a region of the foil where the platinum layer overlaps with the silicon substrate, the evolution of the grain structure of platinum was studied. Grain growth with crystallisation was apparent in the micrographs (Fig. 3.19), with grain size increasing from ~10 nm for the as-deposited sample, to ~30 nm at 500 °C, to ~50 nm at 650 °C. The distribution of grain sizes became more random with increasing temperature. Lattice fringes due to strong crystallisation could be observed within individual grains. In the thinner regions of the specimen, the appearance of voids was observed, with the formation of grain clusters (group of 15-25 grains). The size and distribution of the clusters appears to relate to the platinum-silicon islands observed in the cross-sectional micrographs (Fig. 3.18).

Figure 3.20: Schematic depicting proposed mechanism for platinum-silicon reaction, based on in situ plan view TEM analysis and cross-section TEM analysis with EDX.
Energy dispersive X-ray analysis (EDX) carried out on the cross-section specimens indicated that the island regions consisted of platinum and silicon. The regions between the islands had an upper surface (with a speckled appearance in the micrographs) rich in titanium and oxygen, while the layer below was predominantly platinum and silicon. This lead to the conclusion that the mechanism schematically depicted in Fig. 3.20 prevails. As grain growth in platinum is initiated, titanium diffuses to the regions at the grain boundaries. This titanium is exposed to oxygen in the sputtering gas mixture and forms a stable oxide of titanium. As temperature increases platinum reacts with silicon forming islands of silicide, with regions of titanium oxide present in between (the oxide form presumably prevented the formation of titanium silicide). The presence of all four elements – Si, Pt, Ti, and O – was confirmed using Auger electron spectroscopy depth profiling. During subsequent deposition of PSZT, it appears to preferentially grow on the regions with platinum, resulting in the final island-structure observed in the film.

3.5.3 Section conclusions

PSZT thin films deposited on Pt/Ti/Si were analysed using transmission electron microscopy based techniques. This analysis was motivated by potential uses of possible island structure in the film, as a result of roughening of the bottom electrode surface. TEM analysis confirmed the presence of platinum-silicon islands, on which preferential growth of PSZT was observed, resulting in a non-continuous island-structured film. Efforts were made to understand the mechanism of formation of the islands of platinum and silicon, using a combination of plan view TEM with in situ heating and EDX analysis on cross-sectional TEM specimen. A possible mechanism for this island formation has been identified.
3.6 Conclusions

Extensive materials characterisation of PSZT thin films deposited on gold and platinum coated silicon substrates has been carried out. The focus has been on silicon substrate based studies, in order to enable future incorporation of PSZT thin films in silicon-based devices. Spectroscopy and microscopy techniques were used, often in combination, to study the microstructure of the deposited thin films.

During the course of the materials characterisation carried out, the following key results have been obtained:

A. The films were found to be of the same composition as the target, with the chemical composition staying uniform through the film thickness.

B. The evolution of grain structure of PSZT on gold and platinum coated silicon substrates has been analysed, with any observed trends recorded.

C. Conditions for achieving least stress in multi-layer structures with PSZT have been identified.

D. The presence of columnar grain structure in all the preferentially oriented thin film structures has been observed. The columnar grains were very well defined in the case of PSZT on Pt/TiO₂/Si, with high aspect ratio columns.

E. In certain cases, undesirable metal-silicon reactions were observed, with an effect on the final PSZT film microstructure. Efforts have been made to explain the underlying mechanism for these reactions.

F. A guiding effect of gold on PSZT, due to similar lattice spacings, was hypothesised. This guiding effect of (111) Au on (104) PSZT was observed by high resolution transmission electron microscopy and verified using crystal structure simulations.
4.1 Introduction

The piezoelectric effect is exhibited by the category of materials in which charge is generated when the materials are under stress. The inverse or converse effect also exists; whereby, the materials undergo dimensional deformation when exposed to an electric field. The piezoelectric response is quantified using charge and voltage coefficients. This enables comparison between the piezoelectric behaviour of different piezoelectric materials. One such coefficient is \( d_{33} \), which numerically describes the resulting effect for an applied cause along the same direction. The subscript ‘3’ nominally corresponds to ‘z’ in the standard axis system. Under the direct piezoelectric effect, when a force is applied along direction ‘3’ (equivalent to stress experienced by this direction), a quantity of charge results along this direction. In this case, \( d_{33} \) has the units of pC/N. Under the inverse piezoelectric effect, when a voltage (or an electric field) is applied along direction ‘3’, the dimension of the material along this direction changes. In this case, \( d_{33} \) has the units of pm/V.
A schematic representation of the direct and inverse effect, with respective $d_{33}$ computations, is shown in Fig. 4.1. Though $d_{33}$ is described under these two effects, and with two different units, the numerical value in both cases has been shown to be the same based on Maxwell’s thermodynamic principles [4.1]. This law breaks down in the case of thin films, due to the substrate clamping effect on such two-dimensional structures [4.2], where the length and width dimensions are significantly greater than the thickness.

![Diagram](image)

**Figure 4.1:** Two-dimensional schematic of (a) the direct and (b) the inverse piezoelectric effects. The corresponding expressions used to calculate $d_{33}$ are shown.

When applying existing $d_{33}$ measurement techniques to thin films, numerous challenges were faced, considering the small variations (in charge or displacement) expected from the thin films. The most commonly reported approach, with an ever increasing number of publications each year, is piezoresponse force microscopy (PFM) [4.3]. PFM uses atomic force microscopes (AFM) with additional options: to apply an electric voltage through the tip, which is generally metal-coated to make it conductive; to access signals from the four-quadrant laser detector; electronics to process these signals; and software configuration to map these results as images. PFM excels in relative mapping to study piezoelectric response variations, but is only semi-quantitative in $d_{33}$ measurements. Approaches for quantitative measurement of $d_{33}$...
have been demonstrated using nanoindenters by Koval et al. [4.4], under the direct piezoelectric effect.

Using PSZT and reference thin film materials – amorphous silicon dioxide (non piezoelectric) and aluminium nitride (standard piezoelectric) – two new and relatively simple techniques for piezoelectric response estimation have been developed. The techniques aimed to enable piezoelectric response estimation using standard equipment, such as the nanoindenter and atomic force microscope, without the need for extensive modifications or additional options.

The capabilities of the techniques described in this chapter have been demonstrated using PSZT thin films deposited on gold-coated silicon substrates. Basic details on the films deposited are provided. Discussions with respect to the measured thin film piezoelectric response values using these techniques are carried out in Chapter 5 of this thesis.

### 4.2 Sample Preparation for $d_{33}$ Measurements

The need to use standard equipment necessitates a couple of additional steps in preparation of samples for $d_{33}$ measurements. To estimate the piezoelectric response of the deposited thin films in terms of $d_{33}$, samples were fabricated to form a sandwich electrode structure. The following sample preparation description applies for any film to be studied, but has been described with reference to PSZT.

During PSZT deposition, a portion of the bottom metal electrode (gold or platinum) was covered with a piece of silicon to prevent sputtering of PSZT on the selected region of the sample; this was done to create electrical access to the bottom
electrode. This form of shadow masking was performed in order to study the film in its as-deposited form, without exposing it to wet chemical etchants. The top metal electrode (600 nm aluminium) was deposited at room temperature by electron beam evaporation. In this case also, evaporation was carried out through a shadow mask with small openings to define the top electrode. On all samples, two or more electrodes were defined to study the uniformity in response of the thin films. Individual samples were firmly mounted onto glass slides using non-conductive double-sided tape. The glass slides used had gold islands defined by photolithographic patterning, with the gold having been deposited by electron beam evaporation (at room temperature) to a thickness of 150 nm, using a 15 nm titanium adhesion layer. The top and bottom electrodes were wire-bonded to individual gold islands on the glass slide using gold ribbon (76 μm wide and 12.5 μm thick). Fine gauge wire was bonded using silver epoxy to these gold islands, to serve as connectors to external devices, such as the function generator. All connections were tested to ensure that no electrical shorts were present. A schematic representation of such a sample is shown in Fig. 4.2.

Figure 4.2: A schematic representation of samples prepared for piezoelectric response measurements. (Not to scale)
4.3 Estimation of $d_{33}$ using a Nanoindenter

Published work on the measurement of the piezoelectric response of thin films using a nanoindenter [4.4-4.7] are generally based on the direct piezoelectric effect, and use the nanoindenter to apply stress on the thin films. While these techniques are expected to give the same numerical value for $d_{33}$, they require an in-depth understanding of indenter mechanics, dynamics, and principles. Whereas, the technique presented below uses the indenter only as a means of accurately measuring displacement. Related work by Rar et al. [4.8] has been carried out for piezoelectric substrates using the inverse piezoelectric effect, and highlights that the indentation approach leads to better quantification of $d_{33}$, compared to the popular piezoresponse force microscopy (PFM) technique.

4.3.1 Experimental details

An UMIS 2000 nanoindenter (CSIRO, Australia) was used to carry out the measurements, given its precision for displacement measurements. A blunt metallic tip was used to prevent deformations to the thin film being tested, and contact of the tip to the film was made with a force of 1 mN. The indenter tip was brought into contact with the surface of the top electrode or the piezoelectric thin film. The piezoelectric thin film studied was PSZT deposited for a duration of 4 hours at 300 ºC on gold-coated silicon substrates (PSZT on Au/Ti/Si with a PSZT thickness of ~1900 nm). A schematic of this arrangement is shown in Fig. 4.3. The top electrode was connected to ground of the function generator. This was done to ensure that no electrostatic interaction between the tip and the sample affected the measured displacements. The indenter software (IBIS, version 1, 2004 from Fischer-Cripps Laboratories Pty. Ltd.) was used to follow the displacement of the surface of the films over time. Most measurements were made by placing the tip on the surface of the aluminium top electrode, to ensure the response to the entire electric field is measured. Low frequency (ranging from 25-500 mHz)
electrical signals with peak-to-peak voltages of 10 V and 32 V were used, due to the limitations in the sampling rate of the software. Mapping options in the software were used to precisely position the nanoindenter tip and perform line scans and area scans to study piezoelectric response variations.

Figure 4.3: Schematic of the arrangement used to measure the piezoelectric response of the PSZT thin films. (Not to scale)

4.3.2 Results

Initial piezoelectric response measurements were done on the surface of the aluminium top electrode, in order to study the response of the piezoelectric thin film to the entire applied electric field. Applied peak-to-peak voltages of 10 V and 32 V at one particular point, resulted in peak-to-peak film thickness changes of 4.34 nm and 13.97 nm respectively. These relate to $d_{33}$ values of 434 pm/V and 437 pm/V respectively, indicating a linear and consistent result. These are typical of results obtained for $d_{33}$ measurements done at different points.
Mapping of the thin film piezoelectric response over an area of 80 μm by 80 μm on the aluminium top electrode showed a region of high piezoelectric response, with the varying response around that region (Fig. 4.4). This is due to the variations in the alignment of domains in the region being studied. A minimum $d_{33}$ value of 458 pm/V and a maximum $d_{33}$ value of 608 pm/V were obtained, with an average value of 545 pm/V.

![Figure 4.4: Results from mapping the piezoelectric response of a PSZT thin film over an 80 μm × 80 μm area (on the aluminium electrode surface) for an applied peak-to-peak voltage of 32 V.](image)

The piezoelectric response was mapped along a line of length 1250 μm, at intervals of 250 μm, and the resulting data is shown in Fig. 4.5. The response is high and reasonably consistent on the top of the electrode, reaches a maximum closer to the edge of the electrode, and drops to a lower value when measured directly on the thin film. These results follow the expected variations in electric field strength. The field is expected to be at its maximum between the top and bottom electrodes, with its
strength decreasing with distance from the electrode area.

Figure 4.5: Results from a linear map of the piezoelectric response for an applied peak-to-peak voltage of 32 V, to study variations in response with distance from the top aluminium electrode.

In order to validate the measurement technique, a sample with the same overall arrangement, but with amorphous silicon dioxide instead of PSZT was tested. The resulting response under an applied electric potential for silicon dioxide was a null response, similar to those obtained when no electric potential was applied to the piezoelectric PSZT thin film. This supports the conclusion that the film thickness variations measured were a direct consequence of the piezoelectric behaviour. The range of $d_{33}$ values was also verified using the technique described in Section 4.4.

4.3.3 Section conclusions

In summary, a technique for quantitative estimation of $d_{33}$ (in pm/V) under the inverse piezoelectric effect has been presented. The measurements were carried out using a nanoindenter, in order to utilise its accuracy in measuring displacements. The
nanoindenter mapping capabilities were used to demonstrate mapping of piezoelectric response over an area and along a line. This technique is described in [4.9].

4.4 Estimation of $d_{33}$ using an Atomic Force Microscope

This section describes a technique for the quantification of $d_{33}$ using atomic force microscopes (AFM), without the need for modifications; to support and simplify other reported techniques, such as piezoresponse force microscopy (PFM) [4.10] and piezo-nano-indentation (PNI) [4.4]. The AFM is used under the standard contact mode imaging settings, as is done for most surface topography scans. Samples are prepared (as described in Section 4.2) to study the piezoelectric response of the thin films under the inverse piezoelectric effect. The technique uses the scan result at a given point to extract the peak-to-peak displacement of the thin film for a specific applied peak-to-peak voltage. This results in a quantified value for $d_{33}$ in pm/V. In addition, piezoelectric response hysteresis loops and electric field induced strain loops can be extracted from the scan data, and the relative performance of films can be compared; sample results for measured hysteresis loops are presented in Section 5.2.

4.4.1 Experimental details

PSZT thin films deposited on Au/Ti/SiO$_2$/Si substrates at 300 °C for 4 hours were used during the development of this technique. These films were subsequently annealed in the sputtering chamber, during the cooling down process, at 250 °C for 1 hour. A Digital Instruments Dimension 3100 atomic force microscope with a Nanoscope IIIa controller was used for these experiments. The instrument was calibrated for ‘z’ displacements before use, using a 100 nm step height standard. The system was used in the contact mode imaging arrangement, with non-conductive silicon nitride tips.
Figure 4.6 is a schematic representation of the testing arrangement used (similar to Fig. 4.3). The AFM tip is placed at a chosen point on the surface of the top electrode. An electric field is applied between the top and bottom electrodes with the top electrode connected to the ground of the function generator to prevent charging up of the non-conductive tip surface (this could cause attractive or repulsive forces, and so, could introduce errors). The electric field in Fig. 4.6 is represented using two components: $V_p$ represents the peak value or amplitude of the signal and is half the peak-to-peak voltage value, and $f(t)$ represents the signal type used and corresponds to the sine function. Frequencies ranging from 500 mHz to 10 Hz were experimented with, limited by the sampling rate and tip mechanics of the system.

![Figure 4.6: Schematic of the arrangement used for piezoelectric response measurements using the AFM. (Not to scale)](image)

All scan results incorporated in this article were carried out with resolution settings of 512 pixels/line and 512 lines in an image. The scan area value is set to zero and the line scan frequency was set to 1 Hz. The electric field was applied using an
Agilent Technologies 33220A function generator without a 50 Ω termination. In order to accurately evaluate the electric signal applied across the film, an oscilloscope was connected in parallel during all measurements.

4.4.2 Results and discussion

This section describes the results obtained using the proposed piezoelectric response measurement technique, and discusses the manner in which the electromechanical coefficient $d_{33}$ can be obtained from the scan results.

Figure 4.7 shows the scan results obtained with a scan rate of 1 Hz and for varying applied signal frequencies, from 1 to 4 Hz. Considering that the AFM tip is not scanning over any region (it is at one chosen point on the top electrode), the displacements observed in Fig. 4.7 correspond to variations in thickness over time at a point chosen on the sample. This is different from normal AFM scan results in which displacements are mapped over a chosen area. Figure 4.7 [especially Fig. 4.7(b)] clearly depicts that every scan line has sinusoidal variations, with the number of cycles directly corresponding to the ratio of the driving frequency (1-4 Hz) and the scan frequency (1 Hz); each sinusoid corresponds to a set of bands (one dark and one light) in the scan result. The bands in the scan result shift for each line, with an overall diagonal appearance; this is a result of delays introduced by the AFM feedback system after each scan line.

This result demonstrates that the thin film displacements occur at the applied electrical signal frequency, as expected. Samples with amorphous silicon dioxide in place of PSZT were tested under the same arrangement and exhibited no displacement variations (null response – only background noise in scan results). This clearly indicates that the displacements being measured are due to the piezoelectric
behaviour of the PSZT thin films.

Figure 4.7: Scan result when the frequency of the applied sinusoidal electric field was varied from 1 to 4 Hz, in steps of 1 Hz, with a fixed peak-to-peak amplitude of 20 V. The dark and bright bands seen in (a) are due to the applied sinusoidal voltage’s positive and negative cycles, respectively. The three-dimensional representation of (a) shown in (b) highlights the sinusoidal nature of the displacement variations.
Figure 4.8: Scan result where three sectors of the image correspond to time periods of no applied signal and to signal frequencies of 1 Hz and 2 Hz for an applied sinusoidal electric field of fixed peak-to-peak amplitude of 20 V.

Figure 4.8 was used to verify the technique further. During the initial portion of the scan, no electric field was applied across the thin film. The result is just background noise in the scan result. On applying an electric field with a frequency of 1 Hz, the film starts to respond instantly, reflected by approximately one sinusoidal cycle in the middle portion of the scan. The number of sinusoids increases to two in the last section of the scan, when the frequency is doubled.

Figure 4.9 highlights the ability of the proposed technique in identifying displacement variations with applied voltage at a constant driving frequency; larger displacements increase contrast in the image while the number of bands in the image remain constant. During the course of the scan, the amplitude of the driving voltage was changed. From an initial peak-to-peak amplitude of 12 V, it was increased to 16 V, with the final scan region being recorded at 20 V. The corresponding peak-to-peak displacements are 1.3 nm, 2.7 nm, and 4.1 nm.
Figure 4.9: Scan result obtained under an applied 4 Hz sinusoidal voltage. The peak-to-peak amplitude of the voltage was increased at regular intervals. The applied voltage and resulting displacement are shown as peak-to-peak values.

From these scan results, the piezoelectric voltage coefficient $d_{33}$ can be estimated in pm/V, as the ratio of the peak-to-peak displacement (in pm) to the applied peak-to-peak voltage (in V). For example, the displacement variations in Fig. 4.9 of 1.3 nm for 12 V, 2.7 nm for 16 V, and 4.1 nm for 20 V, correspond to $d_{33}$ values of approximately 109, 169, and 205 pm/V, respectively (these values are lesser than those for films discussed in Section 4.3 due to lesser degree of preferential orientation). These variations in $d_{33}$ values can be attributed to three factors: (i) higher electric fields tend to increase the magnitude of the piezoelectric response [4.11, 4.12], (ii) non-linear $d_{33}$ variations with electric field due to substrate clamping effects for thin films [4.12, 4.13], and (iii) frequency response variations of the capacitor structure formed for the $d_{33}$ measurements. The values measured by this technique were verified using the nanoindenter-based technique (Section 4.3 and [4.9]); this verified the numerical range of the values but could not be used to confirm exact values as the operating frequency for the nanoindenter-based technique is lower (system limitation). Values in the expected range ($d_{33}$ ~10 pm/V) were obtained for reference aluminium nitride thin films.
4.4.3 Section conclusions

Quantitative estimation of the piezoelectric response using standard contact mode imaging of an atomic force microscope has been demonstrated. The technique has been used to estimate the $d_{33}$ of PSZT thin films deposited on gold-coated silicon samples. This article describes the manner in which $d_{33}$ is quantitatively extracted from an AFM scan image, which is a collection of displacements over time of one point on the sample. The influence of varying electric field parameters, such as frequency and peak-to-peak amplitude, on the piezoelectric response have been successfully studied using the presented technique. The validity of the technique was tested by obtaining a null response for amorphous silicon dioxide samples; expected values for aluminium nitride thin films; and the range of values measured by this technique were verified using the method described in [4.9]. This AFM-based technique is reported in [4.14].

4.5 Conclusions

This chapter presents two new and simplified techniques for the estimation of the piezoelectric charge coefficient $d_{33}$. The following key results have been obtained:

A. A technique has been developed to estimate thin film $d_{33}$ using a nanoindenter under the inverse piezoelectric effect.

B. The capabilities of using the nanoindenter to map piezoelectric response data over an area and along a line, to study influence of electrodes or domain/grain distribution, are presented.

C. An atomic force microscope in the contact imaging mode has been used to estimate thin film $d_{33}$. By following the displacement at one point, a representation of thin film variation as a function of frequency and amplitude of the applied electric field can be studied.
CHAPTER 5

PIEZOELECTRIC RESPONSE RESULTS

5.1 Introduction

The addition of strontium as a dopant to lead zirconate titanate (PZT) has been reported to enhance its piezoelectric properties [5.1-5.4]. These reports have focussed on ceramics and pellets. Having deposited PSZT thin films under optimised conditions (Chapter 2), with extensive materials characterisation carried out subsequently (Chapter 3), these films were studied using the thin film piezoelectric response estimation techniques developed (Chapter 4).

This chapter presents the piezoelectric response results obtained, and discusses the possible sources of the $d_{33}$ values estimated. During the course of $d_{33}$ measurements, certain unique response characteristics for low temperature deposited films on gold and at low frequencies on platinum have been observed. This chapter also describes additional features of the piezoelectric response techniques developed, whereby, data gathered can be used to extract piezoelectric response hysteresis loops.
5.2 Ultra-High Piezoelectric Response Thin Films Deposited at Low Temperatures

Piezoelectric materials are suitable for a wide range of applications such as transducers, actuators, and sensors. They also have created widespread interest given their potential for incorporation in efficient energy scavenging applications, where electrical energy is generated by transforming mechanical energy prevalent in the environment in the form of vibrations (e.g. acoustic vibrations, ultrasonic vibrations, human motion, wind energy) [5.5-5.8]. To realise these applications, high performance piezoelectrics which can be integrated into device fabrication processes are essential. Likewise, to generate appreciable electrical energy from such environmental sources, high performance piezoelectrics and innovative transduction designs need to be employed. The use of piezoelectrics in the form of thin films enables the latter, as microelectronics and/or microsystems fabrication can be utilised to create electrical voltage or power amplification designs, while creating compact devices.

5.2.1 Piezoelectric response of PSZT on Au/Ti/Si

Samples of PSZT on Au/Ti/Si were used during the development of the nanoindenter-based piezoelectric response measurement technique. The results from this analysis are described in Section 4.3.2. This technique was rigorously tested during development to ensure that the values obtained were quantitatively accurate, by ascertaining that similar values were obtained using both the nanoindenter and an atomic force microscope under the same testing arrangement [5.9, 5.10]. Moreover, substrate bending did not influence the results obtained, as no force was applied on the films during testing – identical values were obtained for films deposited on silicon and alumina substrates. The samples were studied under the influence of the inverse
piezoelectric effect, by applying an electric field and observing the variation in the film thickness. More than one top electrode was defined on samples of interest to study the uniformity of the piezoelectric response in different regions of the samples.

Figure 5.1 shows the results from mapping the piezoelectric response over an 80 μm × 80 μm area. A minimum $d_{33}$ value of 458 pm/V and a maximum $d_{33}$ value of 608 pm/V were obtained, with an average value of 545 pm/V. The variations can be attributed to the polycrystalline nature of the PSZT thin film, as a result of which the response is expected to vary across different grains.

Figure 5.1: Results from mapping the piezoelectric response of a PSZT thin film over an 80 μm × 80 μm area (on the aluminium electrode surface) for an applied peak-to-peak voltage of 32 V. (Same as Fig. 4.4)

This measured value of piezoelectric response with a maximum $d_{33}$ of 608 pm/V was, at that time, the highest measured for any piezoelectric thin film deposited on a silicon substrate, compared to the 419 pm/V reported for PZT [5.11]. The high level of
response measured could be attributed to the presence of strontium in the thin films studied, compared to earlier results published for PZT thin films [5.11]; this has been the case reported for bulk ceramics with and without strontium [5.1-5.4]. An additional factor could be low stress in the thin film arrangement, measured to be a compressive stress of 11 MPa. These measurements were performed by estimating the radius of curvature of the samples after thin film deposition, and are discussed in Section 3.2.3 and in [5.12]. The deposition conditions were also chosen to attain high intensity perovskite orientation in the PSZT thin films based on previous work [5.13]; and also from the conclusion that lower deposition temperatures and longer deposition durations result in least stress in the films [5.12].

**Figure 5.2:** The deposition temperature for PSZT on Au/Ti/Si (300 °C) results in a reaction between gold and silicon. The reaction results in the formation of faceted crystallites along the gold-silicon interface (with the thin titanium layer diffusing into silicon). This also results in an amorphous layer of PSZT, at the interface with gold which prevents the crystalline gold from having a guiding effect on the PSZT thin film. The transmission electron micrograph shows detail of one such faceted crystallite. The angle between the (100) silicon surface and the bounding planes of the crystallite is 54.7° confirming that the diffused crystallites are bound by dense (111) silicon planes. The electron beam was parallel to the silicon [110] zone axis.
While this result served as the best $d_{33}$ measurement for a piezoelectric thin film to that date, subsequent microstructural analysis of these films revealed the presence of an undesirable amorphous layer. This was observed during cross-sectional transmission electron microscopy analysis, as discussed in Section 3.2.4. These microstructural characterisation results are summarised using the schematic presented in Fig. 5.2.

5.2.2 Piezoelectric response of PSZT on Au/Ti/SiO$_2$/Si

To prevent the gold-silicon reaction (by fast outward diffusion of silicon) observed in the case of PSZT on Au/Ti/Si, an intermediate silicon dioxide (SiO$_2$, 200 nm thick) layer was introduced between the metal layers and silicon. As discussed in Section 3.3, this had the desired effect of preventing the interdiffusion reaction, resulting in the gold exerting a strong guiding effect on PSZT.

Figure 5.3: Schematic representation of the influence of the inclusion of an isolation layer of silicon dioxide showing the columnar grain structure in the PSZT thin film and the grain growth. *Inset:* The preferentially oriented gold layer has a guiding effect on the PSZT thin film and this high resolution transmission electron micrograph shows the (104) planes of PSZT (with lattice spacing of 0.305 nm) preferentially aligning parallel to the (111) gold planes.
Figure 5.3 is a schematic representation of the marked improvement in the film microstructure as a result of the inclusion of the silicon dioxide layer. The guiding effect of gold on PSZT can be observed in the inset micrograph of Fig. 5.3, where (104) PSZT planes are aligned parallel to (111) gold planes; this is a feature at different points along the interface interspersed with regions of random orientation.

Figure 5.4: Results from two-dimensional mapping of piezoelectric response variations over an 8 μm × 8 μm region on the surface of the top electrode is shown. These response variations can be attributed to the degree of preferential orientation of the grains under test. Mapping results always highlight regions of higher response surrounded by regions of gradually decreasing response. The result shows the change in film thickness for an applied voltage of 32.8 V. The piezoelectric charge coefficient $d_{33}$ (with units pm/V) is estimated as the ratio of these two quantities.

Piezoelectric response measurements on these PSZT thin films on Au/Ti/SiO$_2$/Si samples were carried out using a nano-indenteter to estimate the piezoelectric charge coefficient $d_{33}$. The response variations (as peak-to-peak changes in film thickness)
over an 8 μm × 8 μm region under an applied electric peak-to-peak voltage of 32.8 V for a 1.6 μm thick PSZT thin film sample are shown in Fig. 5.4. This figure shows bands of piezoelectric response variations which corresponded to a minimum peak-to-peak thickness variation of 24.0 nm and a maximum of 29.3 nm, which respectively correspond to \( d_{33} \) values of 732 pm/V and 892 pm/V. These values are typical of those measured for many PSZT thin film samples deposited under the same conditions.

This ultra-high value of \( d_{33} \) (a maximum of 892 pm/V), which is more than two times higher than the maximum value reported for PZT thin films on silicon (419 pm/V) [5.11], is an improvement of 50 % (one and a half times) on the thin film \( d_{33} \) value of 608 pm/V measured previously for PSZT thin films on Au/Ti/Si (Section 5.2.1 and [5.9]). The ultra-high piezoelectric response measured for these PSZT thin films can be attributed to four factors. Firstly, the PSZT thin films were deposited under optimised conditions following extensive analysis (Chapters 2 and 3). Secondly, the inclusion of the silicon dioxide layer improved the degree of preferential orientation in the PSZT thin films, apparently caused by the increased guiding effect from the underlying gold layer (due to suppression of amorphous layer formation and enhanced gold texturing). Thirdly, the high piezoelectric response could be due to the large applied electric field (~20 kV/mm, for 32.8 V across a 1.6 μm thick film) as this has been shown to influence the response or polarisation behaviour of ferroelectric thin films [5.14]. During measurements, it was observed that there was an exponential (and not linear) increase in piezoelectric response values with increasing electric field. Finally, and most importantly, the ultra-high piezoelectric response observed could be attributed to the modified (and expanded) unit cell of the PSZT thin films under study (Section 2.3.1). This larger unit cell creates more room for atomic displacements under an applied electric field [5.15], with the capability of causing higher levels of strain in the PSZT thin films.
The only comparable result demonstrating ultra-high piezoelectric response thin films was reported by Ouyang et al. [5.16]. While their result clearly demonstrates the ability to engineer films to attain high piezoelectric response, the deposition was carried out at 600 ºC on SrTiO$_3$ substrates. The work reported in this thesis demonstrates comparable high piezoelectric response for deposition at 300 ºC on metal-coated silicon substrates. This makes the process compatible with microsystems fabrication using widely accepted silicon technology, which has proved to be a deterrent to the adoption of piezoelectrics into standard processes [5.5].

### 5.2.3 Section conclusions

A maximum $d_{33}$ value of 892 pm/V was measured for these PSZT thin films on Au/Ti/SiO$_2$/Si. This ultra-high piezoelectric response appears to be a result of optimised deposition conditions and modified unit cell of the PSZT thin films. These piezoelectric films are ideal for integration into existing microelectronics and microsystems device technologies, as the substrate temperature during deposition is a relatively low 300 ºC.

The values of $d_{33}$ reported are termed ‘effective values’, as these apply for piezoelectric response measurements carried out on continuous thin films which are two-dimensional (length and width dimensions much greater than the film thickness). Lefki and Dormans [5.17] and Nagarajan et al. [5.18] have shown that the piezoelectric response of such films are damped by substrate clamping effects and in reality would be even higher. Future work can investigate this effect by patterning PSZT thin films by lithographic means to form island structures of different dimensions.
5.3 Colossal Piezoelectric Response in the Millihertz Frequency Regime

Piezoelectric materials have been studied extensively. One may presume that the field has been exhaustively researched; however, it is apparent from intermittent reports on new phenomena observed in piezoelectric (and ferroelectric) materials, that there is much yet to be discovered and understood [5.18-5.21]. This section reports on the results from the investigation of piezoelectric response of PSZT thin films deposited on platinum coated silicon substrates. This investigation was carried out at low frequencies, extending to the millihertz frequency regime. This resulted in the observation of a new phenomenon in piezoelectric thin films, with colossal piezoelectric response in this frequency range.

This observation is valuable as the adoption of piezoelectric and ferroelectric thin films for applications in the field of sensors, actuators, and transducers for biomedical, specimen manipulation, acoustic, electro-optics, and photonics has resulted in new questions about the nanoscale structure and behaviour of these materials.

5.3.1 Piezoelectric response of continuous thin films on Pt/TiO$_2$/Si

Measurements of $d_{33}$ were carried out on samples subjected to the inverse piezoelectric effect – a voltage was applied across the thickness of the film and the corresponding change in film thickness was measured. The measurement techniques, with either a nanoindenter or an atomic force microscope, used for this low frequency piezoelectric response measurement were developed during the course of this program (Chapter 4), and have enabled this study. Both techniques had different frequency regimes of operation, as discussed in Chapter 4. In both techniques, no force is applied on the sample being studied, and this prevents any substrate bending, which is often a
source of concern in measuring $d_{33}$ of thin films under the direct piezoelectric effect. Moreover, to prove that substrate bending does not influence the results, PSZT thin films deposited on both silicon and alumina substrates were tested. Identical results were obtained. Considering the vastly different elastic modulus for silicon and alumina, inaccuracies introduced by substrate bending can be confidently ruled out. Electrode area also did not have a significant effect on the $d_{33}$ values measured.

Initially, as routine $d_{33}$ measurements were carried out, extremely high piezoelectric response results were obtained for measurements using the nanoindenter. These also differed from results obtained using the atomic force microscope. This led to the conclusion that this category of films exhibited strong frequency dependent $d_{33}$ characteristics.

![Piezoelectric Response Results](image)

**Figure 5.5:** Comparison of piezoelectric response coefficient ($d_{33}$) values obtained for different analysis frequency for PSZT thin films on Pt/TiO$_2$/Si. It is apparent that the decrease in frequency results in an increase in piezoelectric response. The square marker denotes data collected using a nanoindenter, the triangles denote data collected using an atomic force microscope, and the circle corresponds to reference data from [5.1-5.4].
Figure 5.5 shows a snapshot of the dependency of the piezoelectric charge coefficient \( d_{33} \) on the driving frequency of the applied electric field, for PSZT thin films deposited on Pt/TiO\(_2\)/Si. An exponential increase in the value of \( d_{33} \) can be observed with decrease in the frequency, for these measurements carried out at room temperature and atmospheric pressure. The exponential dependence shown in Fig. 5.5 was observed only for the films deposited on platinum-coated silicon at high temperatures. This exponential increase at low frequencies was not observed for PSZT thin films deposited on gold-coated silicon (both Au/Ti/Si and Au/Ti/SiO\(_2\)/Si) at 300 °C.

Table 5.1: Piezoelectric response data versus frequency for a sample with PSZT deposited on Pt/TiO\(_2\)/Si. The experimental data provided below has been used to generate the graph shown in Fig. 5.5.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Frequency</th>
<th>Estimated piezoelectric coefficient ( d_{33} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indenter</td>
<td>( 25 \times 10^{-3} )</td>
<td>10,002</td>
</tr>
<tr>
<td>AFM</td>
<td>1</td>
<td>4,353</td>
</tr>
<tr>
<td>AFM</td>
<td>2</td>
<td>3,625</td>
</tr>
<tr>
<td>AFM</td>
<td>4</td>
<td>2,339</td>
</tr>
<tr>
<td>AFM</td>
<td>15</td>
<td>647</td>
</tr>
</tbody>
</table>

Piezoelectric response data is generally collected at 110 Hz, and such standard reference data for PSZT is also shown on this graph [5.1-5.4]. The peak value of \( d_{33} \) obtained corresponding to the data presented in Fig. 5.5 is \(~10,000\) pm/V (the data used to plot Fig. 5.5 is shown in Table 5.1). This value can be termed colossal in comparison to reported data, and is comparable to the colossal \( d_{33} \) value of \(~9,000\) pm/V reported by Wu and Cohen [5.21] for piezoelectric material undergoing anomalous transformations due to pressure and the giant piezoelectric response with
$d_{33}$ of $\sim$2,000 pm/V observed at cryogenic temperatures by Grupp and Goldman [5.19]. This trend, of decreasing $d_{33}$ with increasing frequency (in Fig. 5.5), which appears to plateau (when considered on a linear scale), can also be extended to the MHz frequency regime and was reported using laser interferometry by Zhao et al. [5.22].

![Image of PSZT thin films deposited on Pt/TiO$_2$/Si substrates: (a) Hollow cone dark field cross-sectional transmission electron micrograph showing columnar grain growth and (b) X-ray diffractogram indicating preferential orientation.](image)

**Figure 5.6:** Analysis of PSZT thin films deposited on Pt/TiO$_2$/Si substrates: (a) Hollow cone dark field cross-sectional transmission electron micrograph showing columnar grain growth and (b) X-ray diffractogram indicating preferential orientation.
This colossal piezoelectric response at low frequencies can be explained by the unique structure of these PSZT thin films. (Some microstructural characterisation results from Sections 2.3 and 3.4 are summarised in Fig. 5.6.) These PSZT thin films have a preferentially oriented columnar grain structure. The columnar grain growth is evident in the transmission electron micrograph in Fig. 5.6(a). X-ray diffraction analysis [as in Fig. 5.6(b)] confirmed that the films were preferentially oriented and the growth direction was aligned closely to the $c$-axis of the crystal structure. PSZT generally exhibits a perovskite structure with an $ABO_3$ configuration, with the crystal structure either tetragonal or rhombohedral. For the composition of the PSZT thin films being considered, the rhombohedral form dominates. X-ray diffraction analysis, supported by selected-area electron diffraction, showed that these films had a modified (strained) unit cell [5.23]. While this cell maintained its expected volume, it was significantly longer along its $c$-axis (Table 5.2). This 9.49% elongation of the $c$-axis, accompanied by the decrease in the $a$-axis, results in a unit cell in which the displacement of the atoms being subject to the electric field can be significantly enhanced.

**Table 5.2**: Comparison of crystal structure parameters of modified PSZT unit cell with expected values. The significant strain in the unit cell is apparent from the 9.49% increase of the $c$-axis. This table summarises the results from Section 2.3.4.

<table>
<thead>
<tr>
<th>Unit cell parameter</th>
<th>Expected parameters based on ICDD-PDF 04-002-5985</th>
<th>Experimentally derived parameters</th>
<th>Difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>5.732</td>
<td>5.450 ± 0.010</td>
<td>-4.92</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>14.317</td>
<td>15.675 ± 0.015</td>
<td>+9.49</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>407.36</td>
<td>403.20</td>
<td>-1.02</td>
</tr>
</tbody>
</table>
Piezoelectric force microscopy analysis revealed that these films exhibited relaxor ferroelectric behaviour, with poor charge retention. This was along expected lines, considering the thin film composition. Relaxor ferroelectrics tend to exhibit larger strain under applied electric field [5.20], enabled by reversible ferroelastic domain switching in the materials. This is attributed to the presence of polar micro-regions in these materials [5.20, 5.24]. This results in very slim and low hysteresis polarisation-field loops. Such materials also exhibit polar behaviour above the curie point due to the permanently polar micro-regions, which do not fully transform into neutral cubic phases.

The relaxor ferroelectric behaviour combined with the longer c-axis could account for the colossal piezoelectric response observed. This process was reversible, with no pinning of domains, as the thin films under study returned to their original thickness once the applied electric field was switched off. The piezoelectric response observed is dominated by the ferroelastic domain switching process, which is a relatively slow process relying on domain growth. Thus, slow varying electric fields are more effective in comparison to faster varying electric fields – this enables more domain growth.

5.3.2 Piezoelectric response of island structured thin films on Pt/Ti/Si

If the colossal piezoelectric response observed is due to ferroelastic domain switching (as hypothesised), it should be possible to enhance it by reducing the clamping effect of the substrate on the thin film. Unlike a bulk piezoelectric crystal, grains or domains of the thin films are constrained by neighbouring grains. This limits the ability of the film to be strained under an electric field, and was proposed by Lefki and Dormans [5.17]. A novel and scalable approach was used to form self-assembled islands of PSZT, ranging from sub-micron to nanoscale.
Figure 5.7: Analysis of PSZT thin films deposited on Pt/Ti/Si substrates: (a) Cross-sectional transmission electron micrograph showing the distribution of Pt-Si islands with island-type growth of PSZT preferentially on these islands, (b) a schematic depicting this film structure, and (c) the corresponding X-ray diffractogram.
Figure 5.8: Comparison of piezoelectric response coefficient values ($d_{33}$) obtained at low frequency: (a) Island-structure in PSZT (red) significantly improves the piezoelectric response at 25 mHz, but is lower elsewhere compared to the continuous film (blue) due to lesser degree of preferential orientation, (b) Detailed analysis of piezoelectric response of the island-structured PSZT film in the 5-250 mHz range shows that the trend is followed even in this select region. The square markers denote data collected using a nanoindenter and the triangles denote data collected using an atomic force microscope.
Table 5.3: Piezoelectric response data versus frequency for a sample with PSZT deposited on Pt/Ti/Si. The experimental data provided below has been used to generate the graph shown in Fig. 5.8(a).

<table>
<thead>
<tr>
<th>Technique</th>
<th>Frequency</th>
<th>Estimated piezoelectric coefficient $d_{33}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hz</td>
<td>pm/V</td>
</tr>
<tr>
<td>Indenter</td>
<td>$25 \times 10^{-3}$</td>
<td>35,278</td>
</tr>
<tr>
<td>AFM</td>
<td>1</td>
<td>4,125</td>
</tr>
<tr>
<td>AFM</td>
<td>2</td>
<td>2,332</td>
</tr>
<tr>
<td>AFM</td>
<td>3</td>
<td>1,796</td>
</tr>
<tr>
<td>AFM</td>
<td>4</td>
<td>1,260</td>
</tr>
</tbody>
</table>

This approach was the use of the Pt/Ti/Si architecture, which results in the formation of island-structured PSZT films (Section 3.5), as against the ‘continuous’ films of PSZT on Pt/TiO$_2$/Si. The platinum-silicon reaction and growth of PSZT islands, with columnar grains, can be seen in Fig. 5.7(a, b). The X-ray diffractogram of the resulting structured film shows the main PSZT peak and smaller peaks due to the platinum-silicon reaction [Fig. 5.7(c)]. These structured films also exhibit preferential orientation, although to a relatively lesser degree compared to the continuous PSZT films on Pt/TiO$_2$/Si [Fig. 5.6(b)]. These structured films too have the same modified (or strained) unit cell as the continuous PSZT thin films (Table 5.2).

Piezoelectric response measurements of these samples to estimate $d_{33}$ showed that the response in the millihertz frequency range of these structured thin film samples was significantly higher than that measured for continuous PSZT thin films on Pt/TiO$_2$/Si, as expected. The results obtained are compared in Fig. 5.8(a), with data summarised in Table 5.3. It can be observed that the PSZT films with the island-
structure exhibit relatively lower piezoelectric response (due to weaker preferential orientation) above 1 Hz, but the response increases significantly as unclamped ferroelastic domain switching dominates in the millihertz frequency region.

Closer observation of piezoelectric response in the millihertz frequency regime, down to 5 mHz, shows an increasing response reaching a $d_{33}$ value of about 80,000 pm/V [Fig. 5.8(b), Table 5.4]. This response is 9 times higher than that reported by Wu and Cohen [5.21].

Table 5.4: Piezoelectric response data versus frequency for a sample with PSZT deposited on Pt/Ti/Si. The experimental data provided below has been used to generate the graph shown in Fig. 5.8(b). This sample was subject to shorter duration at high temperature than that for the sample in Table 5.3, resulting in a smaller average size of Pt-Si islands. This experimental work focuses only on the millihertz frequency region.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Frequency</th>
<th>Estimated piezoelectric coefficient $d_{33}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indenter</td>
<td>$5 \times 10^{-3}$</td>
<td>81,808</td>
</tr>
<tr>
<td>Indenter</td>
<td>$25 \times 10^{-3}$</td>
<td>54,018</td>
</tr>
<tr>
<td>Indenter</td>
<td>$50 \times 10^{-3}$</td>
<td>40,067</td>
</tr>
<tr>
<td>Indenter</td>
<td>$250 \times 10^{-3}$</td>
<td>16,028</td>
</tr>
</tbody>
</table>

5.3.3 Section conclusions

The results presented here lend new insight into the behaviour of piezoelectric thin films at low frequencies. The piezoelectric response measured (of ~10,000 pm/V) is greater by a factor of 200, over those normally reported for PZT or doped-PZT compounds. The colossal piezoelectric response observed for continuous PSZT films is explained by the $c$-axis elongated unit cell and the strong ferroelastic domain
switching of these relaxor-type materials. This hypothesis was verified by controlling the growth of PSZT using self-assembled sub-micron and nanoscale islands of platinum silicide, in order to reduce clamping, and obtaining an even stronger piezoelectric response (ranging from \(\sim 35,000\) at 25 mHz to \(\sim 80,000\) at 5 mHz).

This work can be extended much further by creating a relationship between island size and level of clamping, using a number of samples. Further work is required to establish whether this phenomenon also relates to performance under the direct piezoelectric effect. The analysis is currently limited to 5 mHz because of sampling rate limitations, and extension to lower frequencies to identify the point where the increase in \(d_{33}\) stops, will be valuable knowledge.

### 5.4 Hysteresis Loops from Piezoelectric Response Data

![Hysteresis Loop](a)

Figure 5.9 continued ....
Figure 5.9: Extracted piezoelectric response results from one scan line of AFM piezoelectric response data: (a) the applied signal, (b) the resulting change in thickness (the time axis shown is representative, and does not represent the phase relationship between the two sinusoids), (c) the observed hysteresis behaviour (after multiple electric field cycles) in the thickness displacements, and (d) the electric field induced strain in the film.
The piezoelectric response data collected using either the nanoindenter or the AFM can be extracted as ASCII values, using which individual sinusoidal variations can be plotted. To reduce errors in calculation of $d_{33}$ the average of many segments must be used. This data can also be used to create loops to study the piezoelectric hysteresis and the level of strain in the thin film under study as a function of the applied electric field.

An example using data obtained for PSZT on Pt/Ti/Si is shown in Fig. 5.9. Figure 5.9(a) represents the applied sinusoidal voltage of 1 Hz with peak-to-peak voltage amplitude of 3.04 V. Figure 5.9(b) represents the displacement variations of a point on the PSZT thin film. The measured peak-to-peak displacement is 12.54 nm. This corresponds to a $d_{33}$ of 4125 pm/V (row 2 of Table 5.3). By relating the data used to generate Figs. 5.9(a) and 5.9(b), the piezoelectric response hysteresis loop [Fig. 5.9(c)] and the electric field induced strain loop [Fig. 5.9(d)] can be generated. While Fig. 5.9(c) can be generated without additional data, the generation of the strain loop as shown in Fig. 5.9(d) requires accurate estimation of the thickness of the film being analyzed; which, in this case was measured to be 768.8 nm (measured by surface profilometry). The percentage change in film thickness compared to the actual film thickness is then plotted. The piezoelectric hysteresis loop indicates the presence of low hysteresis and near linear response in the change in film thickness for applied electric fields. Fig. 5.9(d) highlights the high level of strain introduced in the film (almost 1 %) and this directly relates to the high $d_{33}$ values measured under the inverse piezoelectric effect. Both Figs. 5.9(c) and 5.9(d) show a response (due to hysteresis) at zero applied electric field, as presented measurements were collected after many cycles.
5.5 Verification of $d_{33}$ values under the direct effect

Cady [5.25] demonstrated using Maxwell’s thermodynamic principles that the numerical value of the piezoelectric charge coefficient $d_{33}$ is the same (in pm/V or pC/N) under the direct and inverse piezoelectric effects. However, Lefki and Dormans [5.17] showed that this was not applicable to thin films.

![Figure 5.10: Initial results from in situ electrical characterisation of a PSZT on Pt/TiO$_2$/Si thin film sample studied using a nanoindenter. Force (shown in black) in the form of a ramp function was applied on the thin film surface, and the generated voltage (shown in red) at that point was measured using a conductive indentation tip.](image)

In order to validate the high piezoelectric response values attained for the PSZT thin films in this thesis, experiments under the direct piezoelectric effect are very valuable. Such experiments could not be extensively carried out during the course of this doctoral program due to lack of access to any equipment which could carry out this task. A lot of work was carried out on replicating experiments by Koval et al. [5.26] in
this regard. This involved the use of a nanoindenter to apply force and measure generated charge or current. This work verified that the films were capable of converting mechanical to electrical energy by the observation of current transients, but was not suitable for quantification, as measurements were affected by poor signal-to-noise ratio.

Recently, initial tests with a more refined system to measure the generated voltage for an applied force using a nanoindenter have produced promising results. A maximum voltage of 40 mV was generated for an applied maximum force of 8 mN (Fig. 5.10). This corresponds to a piezoelectric voltage coefficient $g_{33}$ of 5 Vm/N. This is related to $d_{33}$ by the dielectric constant of the film, which is expected to be between 500 and 2000 $[5.27]$, as $d_{33} = g_{33} \times \varepsilon_r \times \varepsilon_0$. This relationship results in a $d_{33}$ value between 22,135 pC/N and 88,540 pC/N (depending on the dielectric constant), for this measurement performed at 500 mHz on a PSZT on Pt/TiO$_2$/Si thin film sample. This value is higher than that measured under the inverse piezoelectric effect, and is in agreement with the theory proposed by Lefki and Dormans $[5.17]$.

### 5.6 Conclusions

This chapter presents results obtained for the estimation of the piezoelectric charge coefficient $d_{33}$ of PSZT thin films. Piezoelectric response measurements indicate that the PSZT thin films on gold and on platinum exhibit unique characteristics, with very high response. Possible sources for the origin of the piezoelectric response observed have been identified. The following are the major scientific conclusions drawn:
A. A maximum $d_{33}$ value of 608 pm/V was obtained for PSZT thin films on Au/Ti/Si. At that point, it was the highest value for piezoelectric thin films on silicon.

B. The inclusion of the silicon dioxide layer to prevent the interdiffusion in the electrode layers of the Au/Ti/Si structure, results in improved preferential orientation as a consequence of the guiding effect of the gold layer on PSZT. For these films on Au/Ti/SiO$_2$/Si a peak $d_{33}$ value of 892 pm/V was measured. This is double that measured for piezoelectric thin films deposited on silicon substrates (using any thin film layers) [5.11] and a one and half times improvement over PSZT films on Au/Ti/Si [5.9].

C. The ultra-high piezoelectric response for PSZT thin films on Au/Ti/SiO$_2$/Si was obtained for deposition at 300 °C. This relatively low temperature deposition of a crystalline piezoelectric (which is considered difficult to attain [5.27]) with ultra-high piezoelectric response, makes these films easy to incorporate into Microsystems fabrication processes.

D. The investigation of the piezoelectric response of PSZT thin films on Pt/TiO$_2$/Si using the techniques developed led to the observation of colossal piezoelectric response in the millihertz frequency range. This response appears to be a consequence of the domination of ferroelastic domain switching, which is known to cause large response in relaxor ferroelectric ceramics.

E. In order to verify the above hypothesis, island-structured PSZT films, which were obtained on Pt/Ti/Si substrates, were studied. The island-structure reduces clamping of domains, and therefore, a larger piezoelectric response compared to the continuous PSZT films on Pt/TiO$_2$/Si was expected. The results confirmed this to be the case, verifying the proposed mechanism. This resulted in the measurement of colossal piezoelectric
response coefficient values with $d_{33}$ of $\sim 80,000$ pm/V at 5 mHz.

F. The data gathered during piezoelectric response measurements can be used to extract piezoelectric hysteresis loops and electric field induced strain loops. This has been demonstrated using data obtained for PSZT on Pt/Ti/Si.

G. Preliminary results for measurements under the direct piezoelectric effect have verified the range of $d_{33}$ values measured for PSZT on Pt/TiO$_2$/Si.
6.1 Conclusions

This thesis has dealt with the deposition, characterisation, and piezoelectric response estimation of strontium-doped lead zirconate titanate (PSZT) thin films. During the course of this research program, various significant scientific results have been obtained. These results encompass conditions for optimal deposition of PSZT thin films, extensive microstructural characterisation of these thin films, techniques to estimate the piezoelectric response coefficient \( d_{33} \), and results from piezoelectric response characterisation of the PSZT thin films.

A detailed summary of these results is presented at the end of each of the respective chapters or sections. This chapter provides a brief summary of the results obtained in this thesis. These results highlight that there is scope for much more investigation of the properties of piezoelectric thin films, in general, and PSZT thin films, in particular. The scope of such future work is also discussed.
6.1.1 Deposition parameters for PSZT thin films

Investigations were carried out in identifying optimal deposition conditions for PSZT thin films. The influence of oxygen partial pressure, bottom metal electrode choice, and substrate temperature on the composition and crystal structure of the resulting thin films was analysed. Conditions to achieve desired PSZT thin film composition of \( \text{(Pb}_{0.92}\text{Sr}_{0.08})\text{(Zr}_{0.65}\text{Ti}_{0.35})\text{O}_{3} \) have been identified. In studying the influence of oxygen partial pressure on thin film composition, conditions for deposition of controlled lead-rich films have been identified. This will serve as a technique to design film composition in order to overcome lead loss due to subsequent processing. Suitable bottom electrode architectures for device designs and piezoelectric response measurements have also been identified. Two different modified unit cell structures of PSZT, based on the guiding effect of gold (at 300 °C) or as a consequence of temperature (at 650 °C), have been identified. This result, highlighting the existence of two unit cell structures, demonstrates an approach for tailoring the crystal structure of the material.

6.1.2 Characterisation of PSZT thin films

Extensive materials characterisation of PSZT thin films deposited on gold and platinum coated silicon substrates has been carried out. The focus has been on silicon substrate based studies, in order to enable future incorporation of PSZT thin films in silicon-based devices. Spectroscopy and microscopy techniques were used, often in combination, to study the microstructure of the deposited thin films. The evolution of grain structure of PSZT on gold and platinum coated silicon substrates has been analysed, with any observed trends recorded. The presence of columnar grain structure in all the preferentially oriented thin film structures has been observed. The columnar grains were very well defined in the case of PSZT on Pt/TiO\(_{2}\)/Si, with high aspect ratio columns. In certain cases, undesirable metal-silicon reactions were
observed, with an effect on the final PSZT film microstructure. Efforts have been made to explain the underlying mechanism for these reactions. A guiding effect of gold on PSZT, due to similar lattice spacings, was hypothesised. This guiding effect of (111) Au on (104) PSZT was observed by high resolution transmission electron microscopy and verified by crystal structure simulations.

6.1.3 Piezoelectric response measurement techniques

Two new and simplified techniques for the estimation of the piezoelectric charge coefficient $d_{33}$ have been developed. Both techniques subject piezoelectric thin films to the inverse piezoelectric effect. The first technique uses a nanoindenter, to capitalise on its accuracy in measuring nanoscale displacements. The capabilities of using the nanoindenter to map piezoelectric response data over an area and along a line, to study influence of electrodes or domain/grain distribution, have been demonstrated. The second technique uses an atomic force microscope in the contact imaging mode and has been used to estimate thin film $d_{33}$. By following the displacement at one point, a representation of thin film variation as a function of frequency and amplitude of the applied electric field can be studied.

6.1.4 Piezoelectric response measurement results

Piezoelectric response measurements indicate that the PSZT thin films on gold and on platinum exhibit unique characteristics, with very high response. Possible sources for the origin of the piezoelectric response observed have been identified.

A maximum $d_{33}$ value of 608 pm/V was obtained for PSZT thin films on Au/Ti/Si. The inclusion of the silicon dioxide layer to prevent the interdiffusion in the electrode layers of the Au/Ti/Si structure, results in improved preferential orientation as a consequence of the guiding effect of the gold layer on PSZT. For these films on
Au/Ti/SiO₂/Si a peak $d_{33}$ value of 892 pm/V was measured. This is double that previously reported for piezoelectric thin films deposited on metallised silicon substrates [6.1] and a one and half times improvement over PSZT films on Au/Ti/Si (Section 5.2.1 and [6.2]). The ultra-high piezoelectric response for PSZT thin films on Au/Ti/SiO₂/Si was obtained for deposition at 300 °C (which is considered difficult to attain [6.3]), making these films easy to incorporate into microsystems fabrication processes.

The investigation of the piezoelectric response of PSZT thin films on Pt/TiO₂/Si using the techniques developed led to the observation of colossal piezoelectric response in the millihertz frequency range ($d_{33}$ of ~10,000 pm/V). This response appears to be a consequence of the domination of ferroelastic domain switching, which is known to cause large response in relaxor ferroelectric ceramics. In order to verify this hypothesis, island-structured PSZT films, which were obtained on Pt/Ti/Si substrates, were studied. The island-structure reduces clamping of domains, and therefore, a larger piezoelectric response compared to the continuous PSZT films on Pt/TiO₂/Si was expected. The results confirmed this to be the case, verifying the proposed mechanism. This resulted in the measurement of colossal piezoelectric response coefficient values with $d_{33}$ of ~80,000 pm/V at 5 mHz.

### 6.2 Future Work

This thesis aimed to optimise deposition conditions of PSZT thin films, in order to attain high performance piezoelectric thin films. During the course of this investigation, while many research questions were answered, there arose many dimensions to this project which demand further investigation. A few significant topics which can serve as the focus of future research programs are listed below.
6.2.1 Extension of ability to tailor unit cell to other thin films

The ability to tailor the unit cell of the deposited thin film, by accurate control of deposition parameters, can assist in the development of films with designed properties. This applies particularly to asymmetric crystal structure systems, where the degree of asymmetry can be directly related to the physical phenomenon arising as a result (as in the case of piezoelectricity and ferroelectricity). While this ability to tailor the unit cell has been demonstrated for PSZT thin films, there are possibilities for further control of the unit cell of PSZT by choosing other lattice matched or thermal energy conditions. This can also be extended to other ferroelectric or nonlinear materials, such as undoped PZT, barium strontium titanate, and strontium barium niobate.

6.2.2 Refinement of techniques to measure thin film $d_{33}$

The two techniques to measure thin film $d_{33}$ were rigorously tested with non-piezoelectric materials, standard piezoelectric materials, and multiple samples of PSZT. PSZT samples deposited under the same conditions were studied to ensure that results were consistent, and not a random occurrence. Even with extreme care being taken in the development of these techniques, there is always room for further refinement in testing conditions or parameters. The level of resolution achievable in two-dimensional mapping of the piezoelectric response using the nanoindenter could be studied. Additional lock-in amplification techniques to reduce the level of noise in the AFM-based technique could be considered. The frequency limits of both techniques could be tested further.
6.2.3 Verification of $d_{33}$ values under the direct effect

Preliminary results from *in situ* electrical characterisation of PSZT thin films to measure $d_{33}$ under the direct piezoelectric effect were presented in Section 5.5. These results were able to verify the range of the colossal $d_{33}$ values measured for the PSZT thin films on Pt/TiO$_2$/Si.

There is extensive work required in establishing consistency of these results and in refining this measurement approach in using it to verify values obtained under the inverse piezoelectric effect. Moreover, *in situ* measurements of capacitance during application of force will be valuable in accurate quantification of $d_{33}$ under the direct piezoelectric effect.

6.2.4 Development of models for behaviour of polycrystalline thin films

During the course of this doctoral program, extensive experimental work was carried out. A significant portion of the results obtained were explained using theoretical models reported in published literature for piezoelectric single crystal ceramics or epitaxial piezoelectric thin films. This highlighted the need for convincing and detailed models to enable better understanding of preferentially oriented polycrystalline thin films.
REFERENCES

CHAPTER 1


CHAPTER 2


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2.12 Powder Diffraction Pattern Files, International Centre for Diffraction Data (ICDD, formerly the Joint Committee for Powder Diffraction Studies), Newtown Square, PA 19073, Card 04-0802.


CHAPTER 3


3.9 Powder Diffraction Pattern Files, International Centre for Diffraction Data (ICDD, formerly the Joint Committee for Powder Diffraction Studies), Newtown Square, PA 19073, Card 04-0784.


CHAPTER 4


CHAPTER 5


CHAPTER 6


APPENDIX B


**APPENDIX C**


APPENDIX A

EXPERIMENTAL DETAILS FOR MATERIALS CHARACTERISATION

This appendix provides a succinct overview of all instruments used, with the corresponding experimental conditions. Care has been taken to ensure sufficient detail is presented in order to enable repetition of experiments.

A.1 Microscopy

Microscopy tools have been used extensively throughout this research program in order to characterise deposited PSZT thin films and in the development of a technique for the measurement of thin film $d_{33}$.

A.1.1 Atomic force microscopy

The surface roughness and grain sizes of the PSZT thin films deposited were studied using atomic force microscopy (AFM). AFM scans were carried out using Digital Instruments Dimension 3000 series scanning probe microscopes.
The AFMs used were equipped with Nanoscope IIIa controllers. The topography scans were predominantly carried out in contact mode, using non-conductive silicon nitride cantilevers.

**A.1.2 Transmission electron microscopy**

Cross-sectional transmission electron microscopy (TEM) samples were prepared by one of two processes, based on availability to equipment:

i. Cross-sectional TEM specimens were prepared by gluing coated samples face-to-face with backing silicon, using high strength epoxy resin. This was subsequently mechanically polished using a tripod polisher to create wedge-shaped specimens, with final stages of polishing performed on a 1 \( \mu \)m diamond lapping sheet. The specimens were then ion milled to electron transparency at room temperature using 4.5 kV argon ions incident at 5\(^\circ\) (using double beam modulation).

ii. Cross-sectional TEM specimens were prepared by gluing coated samples face-to-face with backing silicon, using high strength epoxy resin. A core (2.3 mm in diameter) was then ultrasonically machined with the interface of interest at the centre of the core. The core was then glued into a brass tube of 3 mm external diameter. This was then sawed into 500 \( \mu \)m thick sections, ground, and ion milled (Ar\(^+\) at 3.5-5 keV at 4-7\(^\circ\), with double beam modulation) to produce electron transparent cross-sectional specimens.

Knowing the silicon wafer normal and by appropriate tilting of the silicon specimen in the TEM, it was possible to ensure that the film was viewed edge-on, during cross-sectional analysis.
PSZT is a ceramic oxide and exhibits the characteristics of a brittle material. This limits the TEM cross-sectional specimen preparation process. During ion milling for specimen preparation, silicon mills significantly faster than the PSZT thin film; this results in the entire film structure falling off, limiting the extent to which the specimens could be thinned.

Plan view specimens for transmission electron microscopy (TEM) analysis were prepared by mechanically grinding away the backing silicon from the film, with the aid of a calibrated disc grinder. The specimens were then ion milled to electron transparency at room temperature using 4 kV argon ions incident at 5º, with dual beam milling from the back surface of the specimen.

The TEM analysis was carried out at an accelerating voltage of 200 kV on a JEOL 2010F TEM equipped with a Gatan Imaging Filter (GIF2001) and an EmiSpec E Vision energy dispersive X-ray analysis (EDX) system.

**A.1.3 Scanning electron microscopy**

Cross-section analysis of the PSZT thin films discussed in Appendix B was carried out on a field emission gun scanning electron microscope (FEI Nova NanoSEM).

**A.2 Spectroscopy**

Spectroscopy techniques have been used during this research program to study thin film composition. These analyses have enabled optimisation of process conditions to achieve desired composition. During microstructural studies, spectroscopy was also used to investigate the presence of gross composition variations.
A.2.1 Energy dispersive X-ray analysis

Two types of energy dispersive X-ray analysis (EDX) were carried out during the course of this program. This analysis is also known as energy dispersive X-ray spectroscopy (EDS).

i  Initial investigations to verify that the deposited thin film composition matched the sputtering target composition, within acceptable levels, was established using the EDX attachment on a scanning electron microscope. The microscope used was a FEI Quanta 200 environmental scanning electron microscope, with analysis carried out at 20 kV and 30 kV. Subsequently, more detailed composition analysis was carried out using other spectroscopy techniques, as described in the following sub-sections.

ii  On TEM specimens, EDX was carried out using the EmiSpec E Vision EDX attachment in the JEOL 2010F instrument. This was used to study gross variations in composition and identify the composition of layers of interest.

A.2.2 X-ray photoelectron spectroscopy

X-Ray Photoelectron Spectroscopy was carried out using a VG Instruments Model 310 Auger/XPS spectrometer. The surface composition analysis was performed on an area of 5 mm × 1 mm using an aluminium $K\alpha$ (Al $K\alpha$) X-ray source with energy of 1485 eV. Carbon peaks were used to calibrate the resulting spectra to account for any surface charging effects.

A.2.3 Secondary ion mass spectrometry

The SIMS analysis was carried out using cesium ions (Cs+) with a primary accelerating voltage of 7.5 keV and a sampling voltage of 4.5 keV ( Cameca 5f dynamic SIMS instrument). Considering the insulating nature of the film, the sample was biased with an offset voltage of +50 V to overcome charging effects. In view of the low
concentration of strontium in the PSZT thin film samples, in some cases, the two major isotopes – $^{86}\text{Sr}$ and $^{88}\text{Sr}$ – were studied to confirm the presence of strontium. The data presented has been normalized with respect to the cesium signal measured.

**A.2.4 In situ micro-Raman spectroscopy**

Raman spectra were registered in backscattering geometry using a Renishaw 1000 micro-Raman system equipped with a Peltier cooled CCD camera and a Leica microscope. An 1,800 lines/mm grating was used for all measurements, giving a spectral resolution of approximately 1 cm$^{-1}$. Excitation sources used were an Ar$^+$ laser operating at wavelength of 514 nm and a He-Ne laser operating at 633 nm. The laser spot was focused on the sample surface using a 50x objective with short-focus working distance at room temperature. For measurements at higher temperatures (20 °C to 350 °C) a Linkam temperature stage and a 50x long-focus objective were used. With these objectives the lateral resolution on the sample was approximately 2 μm and 3 μm for excitation of 514 nm and 633 nm, respectively. The accumulation time at excitations of 514 nm and 633 nm were 200 s and 50 s, respectively. Considering the volume of data gathered, only spectra (and bands) showing significant variations have been included in the figures in this thesis.

**A.3 Other Analyses**

**A.3.1 Thickness and stress measurements**

An Ambios Instruments XP-2 surface/stylus profilometer was used to measure the thickness of the deposited PSZT thin films. In order to enable this measurement, regions of the substrate were shadow-masked during deposition.
The profilometer was also used for measuring the stress in the multi-layer structures, based on the radius of curvature induced in the substrates by the deposited thin films, as described in Chapter 3. The profilometer software was used to perform these calculations based on a least squares fit method. The scans performed were over regions 5 mm long, centred on the sample, at a scan speed of 0.1 mm/s and with a stylus force of 0.05 mg. All stress values presented are the average of two perpendicular scans. Compressive stress has been indicated using negative values and tensile stress using positive values.

### A.3.2 X-ray diffraction

X-ray diffraction analysis was carried out using a Scintag X-ray diffractometer operating with a cobalt X-ray source (at a wavelength of 0.179020 nm). The scans were carried out for a 2θ range of 20º to 60º with steps of 0.02º. Based on the X-ray intensities detected, the diffractometer was used either in the Bragg-Brentano mode or the glancing angle mode, to achieve optimal sensitivity. The collected data were shifted to correspond to the copper Kα wavelength (0.154056 nm) for comparison with the International Centre for Diffraction Data powder diffraction pattern files available.

### A.3.3 In situ X-ray diffraction

A PANalytical X'Pert Pro diffractometer was used to carry out the in situ X-ray diffraction measurements. The diffractometer operated with a copper Kα source and was equipped with a heating and cooling stage (comprising of a strip of platinum) which enabled recording of diffractograms at different temperatures. The desired temperatures and dwell times were programmed prior to the start of the analysis, and the analysis was carried out in high purity argon. Considering the volume of data gathered, only diffractograms (and 2θ ranges) showing significant variations have been included in the figures in this thesis.
APPENDIX B

PSZT THIN FILMS ON SILICON DIOXIDE

B.1 Introduction

There is potential for harnessing the nonlinear properties of ferroelectric (and piezoelectric) thin films for applications in photonics and integration with left-handed materials (metamaterials). These applications demand that these thin films are deposited on dielectric and optically transparent material. One of the most desirable dielectric layers for the deposition of ferroelectrics is silicon dioxide (SiO$_2$), considering its thermal stability and suitability for optical applications.

Lead zirconate titanate (PZT) is the most commonly used ferroelectric material in commercial applications and results on characterisation of PZT thin films have been extensively reported. While deposition of thin films of PZT on SiO$_2$ has been investigated [B.1, B.2], attaining perovskite structured $c$-axis (columnar) growth directly on SiO$_2$ has proved to be a challenge. Excellent approaches using intermediate layers to seed or control the subsequent PZT deposition have been proposed [B.1, B.2].
While these result in c-axis oriented PZT films, the use of seed layers demands additional deposition steps and access to materials. Most importantly, an additional layer needs to be incorporated into models used to simulate nonlinear characteristics. In this appendix, the deposition of columnar doped-PZT (PSZT) thin films on SiO$_2$, using optimised deposition conditions is demonstrated, overcoming the need for intermediary seed layers. The growth of perovskite structured nanocolumnar strontium-doped PZT (PSZT) thin films is reported. This follows on from the work carried out during this doctoral program, and uses strontium-doped PZT, rather than undoped PZT, which will enable utilisation of its enhanced ferroelectric and piezoelectric properties [B.3-B.5], which in turn will influence its electro-optic performance.

**B.2 Results and Discussion**

PSZT thin films were deposited under conditions as determined in Chapter 2. The deposition was carried out for a duration of 3 hours, on (100) silicon substrates with 300 nm of thermal silicon dioxide. The films were found to be 800 nm thick using an Ambios XP-2 surface profilometer. Characterisation of the thin films was carried out using a combination of techniques, the experimental details of which are described in Appendix A.

PSZT thin films were deposited either at room temperature followed by an annealing process or at a substrate temperature of 700 ºC. PSZT thin films deposited at room temperature were subject to post-deposition furnace annealing at 700 ºC for 3 hours in the presence of high purity argon. In the case of samples deposited at temperatures of 700 ºC, the samples were heated to the deposition substrate temperature at a ramp rate of 10 ºC/min and cooled, subsequent to deposition, at 5 ºC/min; based on previous work [B.6].
B.2.1 X-ray diffraction analysis

Figure B.1: X-ray diffractograms obtained for PSZT thin films on SiO$_2$/Si: (a) deposited at room temperature with subsequent furnace annealing at 700 °C for hours and (b) deposited at a substrate temperature of 700 °C for 3 hours.
Thin films were deposited for a duration of 3 hours to attain a target thickness of 750-800 nm. For obtaining films exhibiting suitable ferroelectric properties, thermal processing was carried out (either post deposition or *in situ*). The aim of this processing was to enable crystal growth in the thin films and attain c-axis orientation.

The X-ray diffractogram of PSZT thin films deposited at room temperature and subjected to post-deposition annealing is shown in Fig. B.1(a), and consists of peaks at expected 2θ positions [B.7]. These peaks are characterised by weak reflections and broad peak widths; indicative of weak preferential orientation, limited grain growth, and a nanocrystalline structure.

**Figure B.1(b)** is representative of diffractograms obtained for PSZT thin films deposited at a substrate temperature of 700 °C. Expected perovskite peaks at 2θ of 29.6° and 49.3°, for (104) and (108) orientations, for a rhombohedral PSZT unit cell [B.7] were observed. Smaller peaks obtained at 34.3° and 58.5° correspond to (006) and (300) orientations, respectively. The temperature at which these thin films were deposited was chosen to encourage thermally-driven grain growth and the diffractogram [Fig. B.1(b)] confirms that this resulted in uniform crystal growth, manifested as strong and sharp peaks in the diffractogram. These results, with strong c-axis preference, also promise strong columnar growth in the thin films (discussed in Section B.2.3).

These results indicate that though post deposition annealing encouraged grain growth, only thin film deposition at high temperatures (*in situ* substrate heating) results in strong preferential orientation. The PSZT thin film samples deposited at 700 °C, with promising XRD results, were subject to further analyses.
B.2.2 Atomic force microscopy analysis

AFM surface scan results for a PSZT thin film deposited at 700 ºC are shown in Fig. B.2. The topography images in Fig. B.2(a, b) depicts tightly packed nanocrystalline grains with an average grain size of 80-100 nm. The average surface roughness ($R_a$) of these films, measured to be about 9-11 nm, indicates that the pronounced grain structure is regular. The accentuated faceting of the grain faces is only conveyed by the peak roughness ($R_p$) values measured to be ~90 nm. The polygonal structure of the grains is apparent in the deflection image shown in Fig. B.2(c).

Figure B.2: Atomic force microscopy scan results for a PSZT thin film deposited on SiO$_2$/Si at 700 ºC: (a) 3-D representation of the film surface showing facetted tightly packed grains; (b) topography image obtained over an area of 1 µm × 1 µm; and (c) the deflection image corresponding to (b).
B.2.3 Electron microscopy analysis

Figure B.3: Cross-sectional scanning electron micrographs in (a) and (b) showing the regular nanocolumnar grains spanning the thickness of PSZT thin films deposited on SiO₂/Si at 700 °C (Observed at specimen tilt of 9°).
Cross-sectional scanning electron microscopy (SEM) showed that the films had nanocolumnar grains extending through the thickness of the PSZT thin films (Fig. B.3). The structure and width of these grains matched those expected from XRD and AFM analyses. There are regions where the PSZT grains end abruptly [especially in Fig. B.3(b)]; this was due to the brittle nature of the ceramic PSZT thin films which prevented better sectioning.

Figure B.4: Plan view transmission electron microscopy results obtained for a PSZT thin film deposited on SiO₂/Si at 700 °C at two different magnifications are shown in (a) and (b).

Plan view TEM analysis results for PSZT thin films deposited on silicon dioxide are presented in Fig. B.4. The nanocrystals observed in the images correspond to grain sizes of 80-100 nm for the columnar preferentially oriented grains in the structure. A majority of the grains appear to be triangular in shape. AFM scans confirmed that the grains in the PSZT thin film are densely packed, and this can be observed in the top-left of Fig. B.4(a). In the other region, the ion milling process for the TEM specimen preparation has resulted in numerous regions devoid of material. This is a by-product of the very rough crystalline film surface. Ion milling from the back results in majority of the material being removed, with only the capping regions of the grains left behind.
The thin region of the specimen gives us valuable information regarding the nanostructure of the thin films. Figure B.4(b) shows that the grains vary in size from 80 to 100 nm, with well defined crystalline and polygonal structure. Strong Bragg diffraction from many grains in Fig. B.4 indicates that they share the same orientation. These nanocrystals extend all the way through the thickness of the specimen forming the columnar structure observed in the cross-sectional analysis. Selected area electron diffraction of the plan view specimen showed that the nanocrystals exhibited the expected perovskite structure (not shown here), but were randomly distributed – there was no preferential orientation along the substrate surface (XRD indicated preferential orientation perpendicular to the substrate). A schematic depicting the overall structure of the PSZT thin films deposited on SiO₂ at 700 °C is shown in Fig. B.5.

Figure B.5: Schematic representation of the PSZT thin films deposited at 700 °C on thermal SiO₂, showing the nanocolumnar polygonal grain structure. (Not to scale)
B.3 Conclusions

This appendix presents results from the first instance of deposition of preferentially oriented, nanocrystalline, and nanocolumnar PSZT thin films directly on thermal silicon dioxide. No intermediate seed or activation layers were used between PSZT and SiO₂. A substrate temperature of 700 ºC was found to be suitable for obtaining the desired perovskite structure. This perovskite structure is expected to exhibit ferroelectric properties suitable for investigation of nonlinear properties for photonics and integrated metamaterials applications.

In Chapter 2, it had been concluded that the orientation of PSZT thin films on gold at 300 ºC was unique to those substrates. It was also proposed that the orientation achieved at temperatures of 600-700 ºC could be realised on multiple substrates, with thermal energy dominating the resulting crystal structure. Therefore, the substrate temperature during deposition results in identical crystal structure for PSZT thin films deposited at 600-700 ºC on platinum or silicon dioxide – this is apparent when comparing the X-ray diffraction patterns in Fig. 2.5 and Fig. B.1.
C.1 Introduction

The lead zirconate titanate (PZT) family of compounds, especially undoped PZT, is used in a wide variety of commercial applications. PZT compounds are popular due to the relatively high piezoelectric response exhibited by this class of materials, thereby, enabling more sensitive sensors, actuators, or transducers [C.1, C.2]. The addition of strontium as an ‘A’-site dopant to the perovskite $ABO_3$ structure of PZT (resulting in strontium-doped lead zirconate titanate, PSZT) enhances the piezoelectric behaviour [C.3-C.5]. In addition to the high levels of piezoelectric response, PZT compounds have a relatively high Curie point. Curie point is the temperature above which the unit cell of piezoelectric compounds transforms from asymmetric tetragonal or rhombohedral arrangement to symmetric cubic arrangement; this renders them non-piezoelectric.
Most reports in literature on Curie point studies of PZT or PSZT involve bulk ceramics and pellets [C.1, C.6]. These reports indicate a Curie point for Pb(Zr_{0.52}Ti_{0.48})O_3 of 380-400 °C, with the Curie point decreasing by about 9.5 °C for every atomic percentage of strontium added as the ‘A’-site dopant. In addition, increasing zirconium concentration also has the influence of decreasing the Curie point. From a combination of these two factors, the Curie point for the thin film composition under consideration is estimated to be between 220-280 °C [C.6]. Further variations are possible due to the two-dimensional nature of thin films.

In this appendix, \textit{in situ} measurements using micro-Raman spectroscopy and X-ray diffraction (XRD) techniques have been used to identify the Curie point for polycrystalline PSZT thin films and to determine the temperature at which significant grain growth is activated for room temperature deposited PSZT thin films. Analysis has been carried out on PSZT thin films deposited at room temperature and at 750 °C; these are expected to be polycrystalline and preferentially oriented, respectively. Raman measurements have revealed interesting variations in the thin film transmission properties and XRD results have highlighted some limitations in using this measurement technique to identify the Curie point of PSZT thin films. It must be noted that Raman measurements do not present strong signatures for PZT-type films (as is apparent in the references cited for Raman spectra) and XRD was used in cases where results using Raman spectroscopy were inconclusive.

\section*{C.2 Results and Discussion}

This section discusses the \textit{in situ} analysis carried out on PSZT thin films deposited at room temperature (Section C.2.1) and on PSZT thin films deposited at 750 °C (Section C.2.2). The changes in the thin film crystallinity have been studied
using micro-Raman spectroscopy and Bragg-Brentano XRD.

**C.2.1 PSZT thin films deposited at room temperature on platinum**

![In situ XRD results for a PSZT thin film deposited at room temperature and heated to 750 °C. (a) Sample set of three diffractograms. Unlabelled peaks are a result of a reaction between the bottom electrode layers and silicon. (b) The variations in the relative intensity of the PSZT cubic peak at 2θ of ~31° during cooling, indicating a marked decrease at 325 °C.](image)

**Figure C.1:** In situ XRD results for a PSZT thin film deposited at room temperature and heated to 750 °C. (a) Sample set of three diffractograms. Unlabelled peaks are a result of a reaction between the bottom electrode layers and silicon. (b) The variations in the relative intensity of the PSZT cubic peak at 2θ of ~31° during cooling, indicating a marked decrease at 325 °C.
PSZT thin films were deposited by sputtering on Pt/Ti/Si samples without substrate heating; these films had no prominent XRD peaks, possibly due to inhibited grain growth resulting in a nano-crystalline disordered structure. XRD spectra were obtained at various points during the ramp-up and ramp-down when these samples were heated to 750 °C and cooled to room temperature. Figure C.1(a) shows the peaks obtained before, during, and after the sample was heated to 750 °C. The diffractogram before the heating process only shows peaks for platinum (from the heating stage and from bottom electrode) which are located at 39.40° and 45.88° [C.7]. The heating process resulted in many new peaks in the diffractogram, while also increasing the background in the diffractograms.

The diffractogram at 750 °C looks similar to the one obtained after cooling down, except that peaks have been shifted left (at 750 °C, due to thermal expansion of the lattice). The peaks at 29.54° and 30.67° correspond to shifted PSZT rhombohedral and cubic peaks, respectively [C.8]; the rhombohedral peak is a double peak due to the presence of two symmetries. A peak at 28.87° (which could not be indexed) appeared at a temperature of 600 °C, the rhombohedral 29.54° peak at 275 °C (corresponding to grain growth), and the cubic 30.67° peak at 400 °C. On cooling down, the peak at 30.67° disappears at a temperature of 325 °C, while a new peak at 56.20° appears corresponding to perovskite PSZT.

Additional peaks at 42.67°, 43.04°, and 47.56° correspond to platinum-titanium silicide which forms due to the heating process as the bottom metal layers react. This results in increased roughening of the platinum layer, which in turn results in a rough PSZT film surface, with an average surface roughness of ~20 nm. This undesirable reaction can be prevented by changing the adhesion layer, but does not influence the
phase transformations occurring in the PSZT thin films.

The peak at 30.67° at 750 °C corresponds to the cubic peak for PSZT (31.04°) [C.8], as the peak position shifted due to thermal expansion. This peak appears during the heating process at 400 °C and disappears while cooling down at 325 °C [see Fig. C.1(b)]; this indicates a phase transformation from rhombohedral to cubic and vice versa, and therefore, the Curie point for this sample is in the range of 325-400 °C. The variations in switching temperatures during the ramp up and ramp down cycles could be attributed to Curie point hysteresis; this is often observed in many piezoelectric ceramics [C.1].

![Raman spectra registered in situ on heating a PSZT thin film deposited at room temperature to 350 °C at 633 nm excitation wavelength.](image)

**Figure C.2:** Raman spectra registered *in situ* on heating a PSZT thin film deposited at room temperature to 350 °C at 633 nm excitation wavelength.

Micro-Raman spectra registered *in situ* for such samples under heating from room temperature to 350 °C are shown in Fig. C.2 (excitation wavelength 633 nm). The spectra obtained during the cooling cycle were quite similar and, therefore, are not presented in this figure with the exception of the spectrum obtained at room
temperature after cooling (see the bottom spectrum in Fig. C.2). The pronounced wide peak observed at approximately 600 cm\(^{-1}\) looks quite similar to the Raman spectra obtained by Souza Filho et al. [C.9] for PZT samples with Zr concentration more than 52 %, which was assigned to the rhombohedral phase (although no strong signatures are apparent). It is evident that the broad features in the Raman spectra are getting less pronounced with increase in temperature, which can be related to the partial transition to the cubic phase. No specific temperature indicating complete transition could be identified. The intensity of Raman spectra gathered using 514 nm excitation were weak, and required long exposure durations.

**C.2.2 PSZT thin films deposited at 750 °C on platinum**

PSZT thin films were deposited on Pt/Ti/Si substrates at 750 °C. These samples were subjected to \textit{in situ} unpolarised Raman measurements, which were performed during heating and cooling of the samples in the temperature range from 20° to 350°. Raman spectra registered at 514 nm excitation for one such sample are shown in Fig. C.3. The spectra during both heating and cooling cycles were identical; hence, only the spectra obtained during the heating process are shown in Fig. C.3. A number of narrow peaks located at 138, 152, 260, 310, and 353 cm\(^{-1}\) as well as wide peaks centred at approximately 260, 600, and 800 cm\(^{-1}\) are present in the spectrum registered at room temperature. Most of these bands are slightly shifted to the low frequency side by approximately 5-7 cm\(^{-1}\) with increase in temperature to 350 °C.

For the assignment of these bands a number of different factors need to be taken into account for the samples under investigation, since the position of Raman peaks in these PSZT samples depends on the Zr/Ti ratio, the Sr content, the size and orientation of the grains, and the intrinsic stress in the films. As shown in literature, the addition of Zr, as well as Sr, reduces the Raman frequency for the majority of
vibrational modes observed for crystalline lead titanate [C.9-C.11] and lead strontium titanate [C.12, C.13].

Figure C.3: *In situ* Raman spectra of a PSZT thin film deposited at 750 °C registered on heating at 514 nm excitation wavelength. *Inset*: Raman spectra showing details of the low frequency range.

The presence of narrow lines as seen in the spectra in Fig. C.3 indicates a crystalline or polycrystalline structure in the film. The peaks seen at 138 cm⁻¹ and 152 cm⁻¹ (inset of Fig. C.3) can be assigned to E(LO₂) and A₁(TO₁) symmetries, respectively. Detailed assignment of peak symmetries is not discussed (see Refs. [C.9-C.13]).
On heating these samples, the two main maxima shift to the low frequency side of the spectra. The peak at 520 cm\(^{-1}\) which corresponds to silicon appears on heating to 285 °C and disappears during the ramp-down at the same temperature. This indicates that the films become transparent to visible light at higher temperatures. This temperature range (285-310 °C) at which this variation occurs could correspond to transformation from the perovskite structured phase to a cubic phase. Disagreements between these Raman results and the XRD results in Section C.2.1 (400 °C during ramp-up and 325 °C during cooling down) for the Curie point can be attributed to the fact that Raman probes short-range structural order, while XRD averages the structural order in the entire film thickness. In addition, grain growth activation in the room temperature deposited PSZT sample could have introduced this variation: the Curie point (325 °C) estimated from the cooling down process of the room temperature deposited PSZT shows better agreement with the 285 °C estimated from Raman measurements.

![Figure C.4](image)

**Figure C.4:** The dependence of the Raman peak positions at 138, 152, and 259 cm\(^{-1}\) with temperature for a PSZT thin film deposited at 750 °C on heating to 350 °C and cooling to 20 °C (633 nm excitation wavelength).
Raman spectra obtained at 633 nm excitation (not shown here) are similar to Fig. C.3, except for the presence of an additional peak seen at 259 cm\(^{-1}\) which shows similar behaviour (as the other maxima) and shifts with changes in temperature (which is shown in Fig. C.4). In addition, the intensities of the low frequency bands are larger, due to larger scattering volume from the 633 nm wavelength laser.

### C.3 Conclusions

This appendix has used *in situ* micro-Raman spectroscopy and X-ray diffraction to identify phase transitions in PSZT thin films. For films deposited at room temperature, and which are possibly nano-crystalline in nature, the temperature for activation of grain growth resulting in preferential orientations has been found to be 275 °C using XRD. The Curie point appears to be between 325 and 400 °C. Raman measurements for these samples indicate a rhombohedral structure with partial transition to a cubic phase. For films deposited at 750 °C, Raman measurements showed that the films become transparent to visible light at temperatures above 285 °C; this corresponds to a phase transformation and could correspond to the transition to a cubic phase.

Additional investigations need to be carried out using both techniques on a collection of films deposited at room temperature and high temperatures, in order to draw more definite conclusions. This could not be done during the course of this doctoral program, as the diffractometer required was under repair for over 12 months. This work is significant from an engineering perspective, as it defines the operating range of temperatures for devices incorporating such piezoelectric PSZT thin films.