Different textured PZT thin films grown on a single SiO$_2$/Ti/Pt stack for piezo MEMS applications

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Abstract

For the past two decades piezo MEMS technology are emerging for its low power consumption of ultrasonic sensing and actuation devices for biomedical applications. Still researchers are facing challenges in miniaturization of piezo-MEMS devices. But up-to-date there is no reports on achieving better sensitivity and actuation strength properties in the same piezoelectric material. As piezoelectric materials are anisotropic in nature, for that it is essential to grow different textured PZT thin film on a single silicon substrate. In the present investigation we have demonstrated the simple method of growing different textured PZT thin film with same process condition without introducing any buffer layer on a platinised silicon wafer by wet chemical method. For this two types of modified bottom electrode Ti/Pt stacks have been proposed i.e., mono- and bilayer Pt on a same silicon substrate using lithography techniques. The texture of the PZT thin film grown on these Pt layers shows (111) and (100) preferred orientations. The XPS surface analysis was carried out on both Pt surfaces to investigate the anomalous behaviour of different textured PZT on different Pt layers. The measured ferroelectric and piezoelectric properties has shown low remanent polarization and high piezocoefficient values for (100) oriented film as reported. The (100) oriented film shows piezocoefficient ($d_{33}$) value twice than that of (111) oriented PZT thin films on a single silicon substrate.

1. Introduction

A great deal of the progress in ferroelectric materials since the 1980’s has been in the field of thin films as compositions developed in bulk ceramics [1-3]. Lead Zirconate Titanate (PZT) is the best known piezoelectric material with superior ferroelectric and piezoelectric properties at its MPB [4,5]. In bulk mode it is widely used by sensor and actuator industries, but recent development in thin film makes it compatible for piezo-MEMS device fabrications [6, 7]. The recent integration of Piezoelectric Micromachine Ultrasonic Transducers (PMUT) into microfluidic channel leads to online monitoring as fluid density sensor, photoacoustic imaging in various industrial and health care applications [8-11].

The functional properties of piezoelectric material vary for sensors and actuators applications. As the sensitivity (as sensor) and actuation strength (as actuators) depends on orientation, remanent polarization, coercive field, permittivity and piezocoefficient values of piezoelectric materials, growing both types of piezoelectric thin films in a single chip silicon wafer is quiet challenging.

In the recent year’s researchers are showing keen interest towards preferential growth of PZT thin films [12], as piezoelectric materials are anisotropic in nature. It is reported that the transverse piezoelectric properties ($e_{31}$) of (100) tetragonal is quit larger than (111) rhombohedral and (110) orthorombic crystal structure of PZT thin films [13,14]. The growth of epitaxial or preferential thin films on platinized silicon wafer is the challenging task as it is based on lattice matching layer with the underlying substrates[15].
Few groups also demonstrated different oriented PZT thin films by tuning the process parameters, composition and annealing conditions etc., on different substrates [16, 17] but it is not possible to grow different oriented PZT under equivalent process condition on a single silicon chip. For the past two decades many reports on preferential growth by using different types of lattice matching buffer layers to achieve higher piezoefficient properties of PZT thin film [18-20]. But introduction such buffer layers has few drawbacks i.e., sometime it will act as a ferroelectric dead-layer at the bottom electrode interface, thus increases the coercive field and degrade other functional properties [21, 22]. It is also reported that the bottom electrode act as the nucleation site for the growth of highly oriented ferroelectric or piezoelectric thin films [23, 24]. This shows the importance of bottom layers on deciding factor for the nucleation sites in particular orientations. Other issues researchers are facing in Ti/Pt stack is formation of hillocks and porosity after post annealing process [25, 26]. This also degrades the bottom electrode quality and subsequently reduces ferroelectric and piezoelectric properties.

In the present study we have investigated the growth of differed textured (111) and (100) oriented PZT film without any buffer layers on a single SiO$_2$/Ti/Pt substrate. In this study we have also addressed the degree of porosity on the Pt stacks using the modified bilayer Pt stack and subsequently tried to understand the nucleation behaviour for the preferential growth of PZT thin film. The comparative study on the nucleation, crystal structure and its ferroelectric and piezoelectric properties of PZT thin film has been well established in this work.

2. Experimentation

2.1 Preparation of bottom electrode stack;

For this investigation two types of Ti/Pt bottom electrode stacks has been prepared by DC sputtering technique (Tecport, target size – 3-inch) on SiO$_2$ substrates. The schematic diagram of layer thickness and the sequences for the preparation of both mono and bilayer Pt stacks were shown in Fig. 1.

![Fig. 1 Bottom electrode SiO$_2$/Ti/Pt stacks (a) Pt_1 (b) Modified bilayer Pt_2 (c) Schematic representation of layer-by-layer stack preparation (d) optical image and (e) AFM images of different textured PZT thin film on a single silicon substrate](image-url)
Initially the mono layer Pt_1 has been prepared by depositing Titanium and Platinum without breaking the vacuum at room temperature. The mono layer Ti/Pt undergoes first post annealing process at 700 °C for 1hrs in conventional furnace. The second bilayer 50 nm Pt_2 film is deposited over mono layer Pt as patterned using lithography techniques and again it was annealed at 700 °C for 30 mins in conventional furnace. The deposition parameters and stacks thickness were given in Table. 1.

Table 1: Deposition parameters for different bottom layer stacks

| Metal     | Thickness (nm) | Pressure (Torr) | Ar (sccm) | power (W) |
|-----------|----------------|-----------------|-----------|-----------|
| Base      |                | Base Deposition |           |           |
| Ti        | 20             | 1.5 x 10^-6     | 6 x 10^-3 | 50        |
| Mono layer(Pt_1) | 130         | 1.5 x 10^-6     | 6 x 10^-3 | 50        |
| Bilayer (Pt_2) | 30          | 1.5 x 10^-6     | 6 x 10^-3 | 50        |

2. Preparation of PZT thin film:

The stoichiometric composition of Pb(Zr0.52Ti0.48)O₃ solution has been prepared by the recipe reported elsewhere [27]. The prepared sol solution was spin coated on the modified mono and bilayer Pt stacks on a single silicon substrate at same process conditions. The spinning rate was 4000 rpm for 30 s and sequentially undergoes pyrolysis at 400°C for 2 mins followed by RTP at 650°C for 2 mins. The process cycles were repeated for 12 times to get the desire thickness of ~700 nm. Finally, the PZT thin film was annealed at 700°C for 15mins in a conventional furnace at ambient atmosphere. In order to confirm the PZT film thickness the wet etching method is carried out using lithography technique and measured by using Dektak XT surface profiler (Bruker) and it was found to be ~700 nm on both the films.

The phase formation of the prepared films was examined by X-Ray Diffraction (XRD) (Rigaku SmartLab, Cuka, λ=1.54Å) and Fourier Transform Infrared spectroscopy (PerkinElmer), Scanning Electron Microscopy (SEM) (Zeiss Gemini monoCL) was taken for microstructural evolution and X-ray photon spectroscopy (XPS) (Axis Ultra 165) for surface analysis. Residual stress measurement (kSA-MOS ultrascan) and ferroelectric properties by Radiant ferroelectric tester and piezoelectric by Piezo Force Microscope (Bruker Model: ) All the measurements were carried out at room temperature.

3. Results and Discussion

3.1 X-ray diffraction analysis:

Figure 2a shows the rocking curve XRD of mono layer (Pt_1) and bilayer (Pt_2) to determine Pt orientation quantitatively. For this the omega scan was carried out at the fixed angle of 0 = 19.9° and 20 = 39.8° corresponds to Pt (111) orientation. The Gaussian fit on the XRD pattern of Pt shows FWHM values of 9.5° and 6.4° for Pt_1 and Pt_2 respectively. From these FWHM values it is well clear that the bilayer stack shows highly oriented Pt than Pt_2. The reason behind this variation in FWHM might be associated with the diffusion of Ti into Pt layer and thus degrade the Pt quality after post annealing process in the case of Pt_1. This result also states that it is quite possible to control the concentration of TiO₂ on to the Pt surfaces as this will act as nucleation site for preferential growth of ferroelectric thin film. The XPS surface analysis was carried out on both the Pt_1 and Pt_2 to confirm the trace of TiO₂ molecules on Pt_1 surface and has been discussed in the lateral section.
Figure 2c and 2d shows 0/2θ normal XRD pattern of PZT thin film deposited on Pt_1 and Pt_2 on a single silicon substrate. The observed peaks were indexed using JCPDS card no: 33-0784 belongs to P4mm tetragonal PZT perovskite system [28]. The XRD pattern of PZT thin film deposited on both Pt layers shows polycrystalline in nature and it has also shown preferred textured w.r.t the Pt layers. The XRD peaks of PZT thin film shows prominent peak at (111) for Pt_1 and (100) orientation for Pt_2 on a single silicon substrate. In general, the surface energy of (111) PZT is lower on SiO₂/Ti/Pt(111) as compared to (100) PZT, hence the growth of (111) PZT is kinetically favored.

![XRD pattern of PZT thin film on Pt_1 and Pt_2](image)

**Fig. 2** XRD pattern of (a) rocking curve on Pt_1 and Pt_2 (b) PZT on Pt_1 (c) PZT on Pt_2 stacks

It is believed that during post annealing process of Ti/Pt thin film the Ti will diffuse through the Pt grains and reaches the surface of Pt, which act as nucleation site for (111) PZT thin film [29-31]. It is also reported that presence of Ti on Pt surface favours (100) whereas TiO₂ favours (111) oriented PZT thin films [29]. But the kinetics behind the (100) preferential growth of PZT on Pt_2 is still not clear [32]. It is reported that the PZT with higher Ti content in Zr/Ti ratio (40/60) and excess PbO at the Pt/PZT interface leads to (100) orientation [33]. But in this scenario the different textured PZT thin film growth took place simultaneously under same process conditions. Among the different (100), (110) and (111) oriented planes, the one with lowest activation energy favours (100) PZT crystal growth in Pt surface [33]. In the absence of any micro crystallization pyrochlore phase (like TiO₂) on Pt surface leads to rapid growth of preferred (100) oriented PZT thin film than other [16]. The degree of crystal orientation was calculated from the expression as follows.

\[
\alpha(100) = \frac{I(100)}{I(100) + I(110) + I(111)} \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots 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The calculated degree of crystal orientation is given in Table 2. From Table 2, it is clear that the different textured PZT thin film grown on Pt_1 and Pt_2 in a single silicon substrate. This preferential growth will have impact on its mechanical and electromechanical properties of the respective PZT thin films.

### Table 2: Relative intensities of (100) (110) and (111) peaks of PZT_1 and PZT_2 on different Pt layers

| Film          | α(100) | α(110) | α(111) |
|---------------|--------|--------|--------|
| Pt_1 (PZT_1) | 2.85   | 3.26   | 93.8   |
| Pt_2 (PZT_2) | 87.21  | 5.11   | 7.67   |

3.2 Microstructure analysis;

![Fig. 3 SEM and AFM images of (a) Pt_1 (b) modified Pt_2 (c) (111) PZT film on Pt_1, (d) (100) PZT film on Pt_2 stacks (e) AFM topography of PZT_1 and (f) AFM topography of PZT_2](image)

Figure 3a and 3b shows the SEM microstructure images of Pt_1 and Pt_2 thin films. It is clearly seen from the SEM images the degree of porosity is higher in Pt_1 compared to modified bilayer Pt_2. The degree of porosity after post annealing of Pt thin film might be associated with the excess unreactive Oxygen/Argon gas trapped within Pt grains [35]. The thickness of the first layer Pt film (Pt_1) is around 120 nm, whereas it is only 30 nm in the second layer Pt film (Pt_2), so the trapped Ar gas will be higher in Pt_1 than the lateral case. In Pt_2 there is still porosity exist but very less compared to Pt_1 film. Another factor to be considered is the stress developed...
during thermal annealing. It is experimentally observed that as-deposited Pt thin film is in compressive stress (~580 MPa) whereas it is in tensile stress (+1.2 GPa) after post annealing process. The reason for the difference in thermal stress state after post annealing might be due to difference in thermal expansion coefficient of underneath Ti and Pt (Pt: 9 x 10^{-6} K^{-1}, Ti: 4.8 x 10^{-6} K^{-1}, Si: 2.6 x 10^{-6} K-1) but the effect is negligible when compared with Si. The average grain size is in the range of 150 to 200 nm, as there is no much difference in the grain size for both the Pt thin films. From Fig. 3b, it is seen that the deposition of second layer Pt doesn’t affect the grain size but reduced the degree of porosity in Pt_2. Overall results clearly indicate that the bilayer Pt shows porous free microstructure for growing quality ferroelectric thin films.

Figure 3c and 3d shows the microstructure of PZT thin film on Pt_1 and Pt_2 respectively. Both the PZT thin film shows well-defined grain boundaries with few porosities in PZT_1 film as expected. The different textured PZT thin film shows different grain boundaries and grain sizes. The distribution of grain size was determined from the grain count using imageJ software and Gaussian fit predicts the average grain size for both the films to be 131 and 250 nm for PZT_1 and PZT_2 respectively. This confirms the importance of bottom layer, acting as a nucleation site for different textured PZT thin films. Figure 3e and 3f shows the AFM topography images of PZT thin film grown on different Pt layer in a single silicon substrate. This will have impact on the ferroelectric and piezoelectric properties of the different textured PZT thin film.

3.3 X-ray photon spectroscopy analysis:

![Image](image.png)

**Fig. 4** X-ray photon spectrum of (a) Platinum (b) Titanium (c) Oxygen of Ti/Pt thin films

The XPS study were carried out to address the presence of TiO_x on the Pt surfaces by determining its oxidation states. Figure 4 shows the Binding Energy vs intensity XPS plots of Pt, Ti and Oxygen on Pt_1 and Pt_2 layers. The intensity and FWHM of the peaks determines the oxidation states and the composition of the films in surface level. From Fig. 4a it is observed that there is no shift in the Pt 4f peak positions at 71 and 74.6 eV corresponds to
Pt\textsuperscript{0} and Pt\textsuperscript{4+} oxidation states of platinum metal. The intense sharp peaks at this region indicates the bilayer Pt\textsubscript{2} qualities are much better than Pt\textsubscript{1}. Figure 4b shows the Ti 2p peaks related to two core level i.e., Ti 2p\textsubscript{3/2} and Ti 2p\textsubscript{1/2} at 458 and 464 eV respectively. The Ti 2p\textsubscript{3/2} peaks at 458.7-458.1 corresponds to Ti\textsuperscript{4+} state and 455.9-455.6 eV corresponds to Ti\textsuperscript{3+} oxidation states of Ti atom [36, 37]. From Fig.4b it is well clear that Pt\textsubscript{2} shows broad asymmetric Ti peaks at 455-458 eV indicates the presence of mixed oxidation states (Ti\textsuperscript{3+} and Ti\textsuperscript{4+}), whereas it is sharp symmetric Ti peak in Pt\textsubscript{1} surface. The intensity of O 1s of oxygen atom at 530.6 eV for Pt\textsubscript{2} is much lower than Pt\textsubscript{1} supports the Ti 2p spectrum. Thus from the above investigation we assign the surface of Pt\textsubscript{1} is accumulated with highly dense TiO\textsubscript{2} and Pt\textsubscript{2} by TiO\textsubscript{x} residuals. It is well clear from the intensity of Pt 4f, Ti 2p and O 1s peaks that the presence of pure state of TiO\textsubscript{2} on the surface of Pt is much higher in Pt\textsubscript{1} compared with Pt\textsubscript{2} layers. This also confirms the presence of TiO\textsubscript{2} on the surface of Pt act as the nucleation site for the (111) preferential growth of PZT thin film on the Pt\textsubscript{1} layer. This TiO\textsubscript{2} nucleation tends to act as a clamping along in-plane direction leads to much tensile residual stress generated in PZT thin film which further decreases or increases its functional properties.

| Oxidation states | Materials | Binding energy (eV) | References |
|-----------------|-----------|---------------------|------------|
| Ti\textsuperscript{4+} | TiO\textsubscript{2} bulk | 459.0 | [36] |
|                  | TiO\textsubscript{2}/Pt (111) | 458.4 | [38] |
|                  | Pt\textsubscript{1} | 458.42 | This work |
| Ti\textsuperscript{3+} | Ti\textsubscript{2}O\textsubscript{3} bulk | 457.5 | [36] |
|                  | TiO\textsubscript{2}/Pt | 456.6 | [37] |
|                  | Ti\textsubscript{4}O\textsubscript{7}/Pt | 456.2 | [39] |
|                  | Pt\textsubscript{2} | 456.76 | This work |
| Pt               | Pt metal | 71 | [38] |
|                  | PtO\textsubscript{2} | 74.9 | [40] |
|                  | Pt thin film | 71, 74.6 | This work |

Based on XPS data we concluded that Ti\textsuperscript{4+} or TiO\textsubscript{2} is present on Pt\textsubscript{1} layer and Ti\textsuperscript{2.5 to 3+} or TiO\textsubscript{x} on Pt\textsubscript{2} layer. In the case of Pt\textsubscript{2} layer the (100) preferential orientation of PZT thin film is due to the low kinetic energy for the growth is preferred in that direction.

3. 4 Fourier transform infrared spectroscopy analysis:

Figure 5 shows the FT-IR absorption spectrum of PZT thin films grown on Pt\textsubscript{1} and Pt\textsubscript{2} layers in a single silicon wafer. The vibrational modes E(3LO) and E(3TO) related to TiO\textsubscript{6} octahedral stretching and bending vibrations are observed at 686 and 537 cm\textsuperscript{-1} of ABO\textsubscript{3} perovskite crystal system [41-43]. Both the films show strong FTIR peaks at this region indicates the non-centrosymmetry in both the textured PZT films. From Fig. 5 it is also clearly observed that there is difference in peak intensity and also significant shift in the peak positions are observed (565 and 520 cm\textsuperscript{-1} for PZT\textsubscript{1} and PZT\textsubscript{2} respectively) in both the films. This indicates the TiO\textsubscript{6} octahedral bending vibration is enhanced in (100) than (111) textured films. This effect will have influence on the piezocoefficient properties of PZT thin films.
3.5 Ferroelectricity and piezoelectricity:

The polarization vs applied voltage is carried out to confirm the ferroelectricity and switching characteristic of the deposited materials. The P-E hysteresis loops were taken for the both the films at 30V, 100 Hz frequency by using Radian ferroelectric tester. Figure 6a and 6b shows the polarization hysteresis loop and switching current of the PZT thin films deposited on Pt_1 and Pt_2 layers on a single silicon substrate. Both the films shown well-defined symmetric hysteresis loop with no significant hysteresis losses. The squareness of the hysteresis loop is higher for the (111) and slanted loop for (100) oriented PZT thin film as reported [44]. The sharp switching current is observed at its coercive field for (111) oriented film.

Fig. 6 (a) Ferroelectric hysteresis loop (b) Switching current and (c) Butterfly strain curve of PZT thin films on Pt_1 and Pt_2 layers
The derived remanent polarization ($P_r$), saturated polarization ($P_s$), coercive field ($E_c$) and switching current of the different oriented films are tabulated in Table 3.

Table 4: Ferroelectric properties of different oriented PZT thin films on different bottom layer stacks

| Stack     | Polarization ($\mu$C/cm$^2$) | $2E_c$ (kV/cm) | switching current (mA) | $d_{33,f}$ (pm/V) |
|-----------|-------------------------------|----------------|------------------------|-------------------|
| Pt_1      | 46.6                          | 83.6           | 152 (+)1.53 (-)2.45    | 420 [This work]   |
| Pt_2      | 23.5                          | 60             | 140 (+)0.58 (-)0.52    | 610 [This work]   |
| PZT(111)  | 50                            | -              | -                      | 71 pC/N [45] [Theoretic] |
| PZT(100)  | $\sqrt{3}$                    | -              | -                      | 189 pC/N [45] [Theoretic] |

It is observed that (111) oriented film shows higher $P_r$ and $P_s$ values than (100) oriented film due to large polarization effect in (111) direction [45, 46]. In (100) oriented film the spontaneous polar axis lies along 35°, whereas for (111) oriented film the polar axis lies along 35°, 74° and 90° normal to the substrate, so the measured maximum polarization value for (100) orientation is expected to be 57% of the original polarization values [46]. The polar axes of the (100) oriented ferroelectric domains are aligning in parallel to the substrates norms as shown in Fig. 7, so that the polarization direction and the field are misaligned to each other leads to low $P_r$ values than (111) oriented film [47]. The low switching current of (100) oriented film also confirm the misaligned ferroelectric domains w.r.t electric field. The pictorial representation of Ti atom position in (001), (100) and (111) oriented ABO$_3$ crystal system w.r.t applied electric field is shown in Fig. 7. It is reported the ferroelectric domains (180°) contribute for higher polarization value whereas ferroelastic domains (90°) contribute of both polarization and strain tensors [48].

Fig. 7 Pictorial representation of Ti atom position in different oriented ABO$_3$ perovskite crystal system w.r.t applied electric field. P-polarization vector, E-electric field direction

In order to study the piezoelectric response butterfly strain loop was measured in Radian ferroelectric tester at 30V, 100 Hz frequency using laser interferometer. Figure 6c shows the butterfly strain vs applied voltage curve of PZT thin films on Pt_1 and Pt_2 layers on a single silicon substrate. The derived effective piezocoefficient ($d_{33,f}$) values from the slope of the butterfly strain loops were given in Table 4. The high $d_{33,f}$ value is shown by preferred (100) orientation than (111) PZT thin film. The theoretically derived polarization and $d_{33}$ values for the (111) and (100) oriented PZT thin films were well matching with our experimental results in the current context [45]. It is reported that the (100) orientation film shows 3 times higher $d_{33}$ values but the mixed (111)/(100) orientation shows 8 times
higher d$_{33}$ than (111) preferred oriented PZT thin films [49, 50]. If we observed the left wing at higher voltage from the plots it is clearly seen the strain curve shows non-linearity for the (111) oriented film, whereas it is linear for (100) orientation. This indicates the contribution of more number of ferroelastic domains in (100) oriented PZT thin films. The low P$_r$ values and low switching current evident the above statement for high piezocoefficient values in (100) oriented PZT thin film. In order to confirm the unforeseen in polarization and piezocoefficient values the PFM studies has been carried out on both the films to study the domain wall contribution if any and discussed in the lateral session.

3.6. Piezo Force Microscopy studies:

The PFM is an extensively used technique to read the domain patterns w.r.t applied voltage to understand the extrinsic domain wall contribution in electromechanical properties. The AFM contact mode was used to study the domain pattern with conducting AFM tip (SIP-PT) act as top electrode for biasing the samples i.e., $V_{tip} = V_{dc} + V_{ac} \sin(\omega t)$ and bottom electrode was grounded. The first harmonic oscillation of the deflected tip was detected as amplitude (tip motion) and phases gives information on the polarization direction relative to electric field. The polarization direction and electric field are parallel to each other resultant out-of-plane displacement and vice versa. Figure 8a and 8b shows the PFM phase images of different textured PZT thin film read at above its coercive field (8V$_{ac}$). From the PFM images it is observed both dark and bright image patterns correspond to downward and upward polarization in the films. From the image lines it is well clear that the (111) oriented film shows at most sharp 180° or 0° domain angle whereas it is of broad non-180° domain angles in (100) oriented PZT thin film. To confirm this phenomena, we have done three box poling effect on both the samples and read with different voltages.

Figure 9 shows the box poling effect on both the PZT thin films. The outer 6 µm x 6 µm box area is poled at (+)10 V, 4 µm x 4 µm is poled at (-)10 v and inner 2 µm x 2 µm is poled at (+) 10 V. The poled films were switched at below (3V, 5V) and above coercive field (8V) to ensure the behaviour of ferroelectric switching related to applied field. Figure 9a-c and 9d-f shows the domain switching of polled (111) and (100) oriented PZT thin films at 3V, 5V and 8V respectively. From the PFM phase images, it is clear that the (111) oriented film retains its poling characteristic even above its coercive field, whereas de-polling effect is seen in (100) oriented film at above coercive field. These results revealed that nanoscale local ferroelectric domain switching is in good agreement to the macroscopic P-E loop as discussed. These also confirms that the polar domain states of (111) oriented films
are in upward direction whereas it is in downward and in-plane direction for (100) oriented film. The upward domains are unstable domains as it may be also an artifacts due to charge injection on to the surface during polling. But the de-polling effect confirm the presence of more stable ferroelastic (non-180°) domains perpendicular to electric field in (100) oriented PZT thin film. Figure 9g and 9h shows the 3D PFM amplitude images for both the textured films measured at 8V<sub>ac</sub> after poling.

![Fig. 9 PFM Phase switching with 2, 5 and 8V<sub>ac</sub> after box poling](image)

The maximum amplitude values were 113 mV and 345 mV for PZT_1 and PZT_2 films. This confirm the enhancement of PFM amplitude in (100) oriented film is from the contribution of ferroelastic domains as said earlier. Figure 10 shows the phase angle domain switching behaviour of PZT_1 and PZT_2 films to confirm this phenomenon.
Fig. 10 PFM Phases loops of (a) (111) and (b) (100) oriented PZT thin films on different Pt layers

4. Conclusion

In conclusion, the different textured PZT thin films have been successfully grown on a single modified bilayer Pt stack by wet chemical methods. The different textured (100) and (111) oriented PZT thin films were confirmed by XRD patterns. The XPS analysis reveals the different nucleation sites (i.e., Ti$^{4+}$ and Ti$^{3+}$) leads to different oriented PZT thin films on a single platinized silicon substrate. The low remanent polarization ($P_r$) and high piezoelectric coefficient ($d_{33,f}$) values were shown by (100) oriented PZT thin film as reported theoretically. The PFM phases and PFM amplitude confirms the contribution of ferroelastic domains in the enhancement of $d_{33,f}$ values in (100) oriented PZT thin film. This new finding removes the barrier in attaining two different textured piezoelectric thin films for better sensitivity and improved actuation strength of piezo-MEMS devices in a single silicon chip. This technology also brings miniaturization and high performance piezo-MEMS devices in the near future.

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