Perceiving nanoscale ferroelectric phenomena from real space is of great importance for elucidating underlying ferroelectric physics. During the past decades, nanoscale ferroelectric characterization has mainly relied on the Piezoresponse Force Microscopy (PFM) invented in 1992, however, the fundamental limitations of PFM have made the nanoscale ferroelectric studies encounter significant bottlenecks. In this study, a high-resolution non-contact ferroelectric measurement, named Non-Contact Heterodyne Electrostrain Force Microscopy (NC-HEsFM), is introduced. It is demonstrated that NC-HEsFM can operate on multiple eigenmodes to perform ideal high-resolution ferroelectric domain mapping, standard ferroelectric hysteresis loop measurement, and controllable domain manipulation. By using a quartz tuning fork (QTF) sensor, multi-frequency operation, and heterodyne detection schemes, NC-HEsFM achieves a real non-contact yet non-destructive ferroelectric characterization with negligible electrostatic force effect and hence breaks the fundamental limitations of the conventional PFM. It is believed that NC-HEsFM can be extensively used in various ferroelectric or piezoelectric studies with providing substantially improved characterization performance. Meanwhile, the QTF-based force detection makes NC-HEsFM highly compatible for high-vacuum and low-temperature environments, providing ideal conditions for investigating the intrinsic ferroelectric phenomena with the possibility of achieving an atomically resolved ferroelectric characterization.

1. Introduction

Ferroelectric materials underpin a broad variety of modern electronic devices, such as ultrasonic sensors, actuators, transducers, ferroelectric memories, and photovoltaic cells. [1,2] Understanding the fundamental mechanisms of ferroelectric phenomena is of great importance in both science and applications. Invented in 1992, Piezoresponse Force Microscopy (PFM) was introduced as a powerful local probing technique to study the properties and phenomena of the ferroelectrics, bringing researchers a great opportunity to perceive the nanoscale ferroelectricity from a real space. [3] After the inception of nearly 30 years, PFM has been developed as a versatile yet indispensable tool to study the local ferroelectricity, piezoelectricity as well as other electromechanical coupling phenomena. [2,4–8] However, the extensive applications and studies of the PFM have revealed a growing number of challenges and concerns about this important technique, which has challenged its...
validity in many studies for a number of years. It has been widely recognized that the two most significant issues faced by PFM are the contact-mode operation and the influences of the electrostatic force. The contact-mode operation can induce pronounced modifications to both sample and tip, such as the surface damage, contamination, charge injection, and triboelectricity as well as the tip wear, contamination, and damage, all of which will affect the PFM signal and may cause significant reproducibility problems and artifacts in the measurements. In addition to the modifications, the tip-sample contact force usually causes a significant stress field in the sample, which can potentially induce a remarkable flexoelectric polarization and affect the ferroelectric polarization switching. Furthermore, as there is a contact area formed at the tip-sample junction which contains a large number of interactional atoms, the contact-mode operation fundamentally limits the spatial resolution of the PFM to the best of sub-10 nanometers, and a higher spatial resolution, such as the molecular or atomic resolution, can hardly be achieved in the conventional PFM. Another important issue closely related to the contact-mode operation is the resonance tracking. As the piezoelectric strain induced by tip electric field is typically with the order of picometers, resonance amplification is necessitated in PFM to enhance the signal-to-noise ratio (SNR) and reduce the AC drive needed. However, a significant concern with the resonance enhancement is that the resonance is highly sensitive to the tip-sample contact status, and a small change of the contact status may cause an apparent influence on the PFM signal. On the other hand, PFM is based on inverse piezoelectric effect and thereby detects the piezoelectric deformation of the sample in response to an external electric field applied between the tip and sample, thus a concomitant electrostatic force will be always involved in the final PFM signal, causing large ambiguity to the interpretation of the measurements. Due to the great importance, a large amount of research work has been implemented continuously to eliminate or quantify the electrostatic force contribution in the PFM measurements but almost all of the proposed solutions, including using stiff cantilever, applying DC compensation voltage, imaging in liquid environment, using higher eigenmode and interferometric detection as well as offline analysis strategies, are subject to specific limitations which have limited the wide applications significantly.

Although the fundamental contact-mode and electrostatic force issues have affected the PFM for several decades, by far the effective solutions are still very limited due to the intrinsic technical limitations, especially when facing the contact-mode issue, and solving these two intractable problems simultaneously are even more difficult. Therefore, to exploit a brand-new scanning probe technique which provides a similar function of PFM and/or detection of the cantilever’s oscillation at two or more frequencies, and these frequency components are usually related to the higher harmonics of the oscillation, higher eigenmodes of the cantilever, and high-order tip-sample interaction, which can be employed to substantially extend the characterization capability of SPM. In this study, by introducing the quartz tuning fork (QTF) force sensor, multi-frequency operation, and heterodyne detection scheme, an excellent candidate for substituting the conventional PFM, which is called Non-Contact Heterodyne Electrostrain Force Microscopy (NC-HEsFM), is developed and introduced here. Similar to that of the conventional PFM, NC-HEsFM also measures the tip electric field-induced surface strain, but via using the new force sensor and detection scheme, a true non-contact yet non-destructive surface strain measurement with significantly minimized electrostatic force effect have been achieved successfully using NC-HEsFM. As it has been generally accepted nowadays that the electric field-induced surface deformation in PFM can originate from multiple mechanisms, the terminology “piezoresponse” in PFM, coined by Gruverman et al. in 1995, may indeed cause misunderstandings when using PFM to study many non-piezoelectric phenomena, a typical example is that the PFM has been renamed as Electrochemical Strain Microscopy when electrochemical Vegard strain is measured. Herein, to avoid such ambiguity, we define any surface strain (or displacement) induced by an external electric field as “electrostrain”. Within this definition, the electrostrain in PFM or NC-HEsFM measurements may arise through a variety of mechanisms including piezoelectricity, electrochemical Vegard strain, electrostriction, measurement-induced electromechanical coupling (e.g., flexoelectric polarization, electrochemical dipole), converse flexoelectricity, Maxwell stress, Joule thermal expansion, and perhaps a mixture of more than one of these effects. In this study, we are focusing on the most important application of NC-HEsFM, that is, the measurement of piezoelectric strain on ferroelectric materials, in which the principle and technical design towards realizing non-contact ferroelectric characterization has been discussed first. Then several conventional ferroelectric materials are used to test the basic ferroelectric domain characterization and manipulation, switching spectroscopy, and multi-eigenmode operation capabilities of the NC-HEsFM. The results show that NC-HEsFM can operate on multiple eigenmodes to perform ideal high-resolution ferroelectric domain mapping, standard ferroelectric hysteresis loop measurement, and domain writing with a true non-contact manner. Meanwhile, the superior non-contact yet real non-destructive characterization and electrostatic force minimization capabilities of the NC-HEsFM have been demonstrated, which are compared with the results from conventional PFM. Finally, the mechanism of achieving effective electrostrain detection by NC-HEsFM has been analyzed using theoretical model and finite element simulations.

2. Results and Discussion

2.1. Non-Contact Detection of Electrostrain

To overcome the issues of contact-mode operation, a natural yet effective solution is to operate the PFM with a non-contact...
mode, but this “simple” idea does become a long-standing challenge in PFM research. To date, only a few attempts of operating PFM with an intermittent contact mode have been demonstrated, whereas the results do show a significant deterioration of SNR and sensitivity as well as a stronger influence from the electrostatic force. Alternatively, conducting PFM measurement with a point-by-point manner has also been proposed to reduce the duration of tip-sample contact however the associated issues of complicated scanning control and much longer imaging time have limited the utilization of this method, and in fact, the electrostrain measurement at each point is still performed via the conventional contact manner. The main difficulty towards achieving non-contact electrostrain detection originates from the significant attenuation of both the electric field located around the tip-sample junction and the tip-sample interaction force with increasing tip-sample distance (will be discussed later). The significant decrease of the electric field strength minimizes the stimulated sample electrostrain while the decay of the tip-sample interaction causes the electrostrain detection sensitivity to decrease pronouncedly, which in turn makes the electrostatic force effect being largely enhanced. Therefore, to achieve an effective non-contact electrostrain measurement, the tip apex should keep a distance from the sample surface as small as possible. However, the theoretical analysis and experiments have clearly demonstrated that, when using conventional cantilever-based tip to perform non-contact scanning at the very near-surface, a minimum amplitude of the cantilever is required to prevent the occurrence of the “jump-to-contact” phenomenon. This minimum amplitude increases when a soft cantilever is used, for example, for a cantilever with medium stiffness of $17 \, \text{N m}^{-1}$, the minimum amplitude is found to be $\approx 34 \, \text{nm}$ at the very near-surface, apparently there is a very large tip-sample separation for effective detection of electrostrain (will be discussed later).

Since the classic cantilever sensor suffers from the fundamental limitations towards achieving non-contact electrostrain measurement, it brings a question that whether is possible to replace this most widely used cantilever sensor with other types of force sensors. The answer is yes, and the QTF sensor is an ideal candidate for it. QTF was introduced to non-contact AFM (NC-AFM) as the atomic force sensor during the end of 1990s and thereafter, the QTF-based NC-AFM has received intensive attention and has been extensively applied to study the most frontier topics of surface science, especially for those systems under extreme conditions (i.e., vacuum and low temperature) where ultra-high spatial resolution can be achieved.

QTF sensor has the advantages of ultra-high stiffness, piezoelectric self-detection capability, and high resonance quality factor (Q factor). The ultra-high stiffness of the QTF prong can eliminate the jump-to-contact effect completely thus allowing the tip to oscillate at the position very near the sample surface even with an ultra-low amplitude. The piezoelectric self-detection capability and high resonance Q factor can provide a much simpler, non-optical, and high-sensitive force detection scheme, which greatly supports the operation of QTF in a variety of environments, including vacuum, ambient, and liquid phase with an ultra-low vibration amplitude. Hence, based on these facts and advantages, it is conspicuous that QTF can be an ideal force sensor that can be used to reach the long-awaited goal of non-contact electrostrain measurement, as it can avoid nearly all the fundamental limitations suffered by the classic cantilever force sensor. Meanwhile, refer to the ultra-high spatial resolution achieved in QTF-based NC-AFM it is reasonable to believe that the current resolution limit of PFM measurement may also get a breakthrough by using QTF sensor under appropriate conditions or environments. Since the traditional cantilever sensor requires a complex optical detection system, using conventional PFM to study piezoferroelectricity under extreme conditions becomes very difficult. In contrast, the non-optical, piezoelectric self-detection and small volume of QTF sensor make it highly compatible for extreme environments, implying that studying the piezoferroelectricity in these environments will be much easier if using the QTF sensor. As the QTF-based NC-AFM also well supports the AFM/Scanning Tunneling Microscopy (STM) dual-mode when using QTF sensor to measure the electrostrain on ultra-thin films, the tunneling current or tunneling spectroscopy can be measured in situ or even simultaneously thus more abundant physical information can be attained. In addition, using QTF sensor for non-contact electrostrain measurement, the large tip-sample junction resistance can reduce the tip-sample current, thereby the influence of Joule heating on electrostrain measurement can also be minimized. Based on the multiple advantages discussed above, in this work, the QTF attached with a conductive nano-tip is introduced as the force sensor to simultaneously measure the topography and electrostrain in a true non-contact manner.

### 2.2. Multi-Frequency Operation and Heterodyne Detection

To achieve the force measurement and feedback control, the QTF needs to be operated in the dynamic mode where a flexural mode of the QTF is typically excited and the corresponding resonance parameters, that is, the resonance amplitude, phase, and frequency, are monitored as the control signal. For most of the previous studies, the 1st flexural mode of the QTF is utilized to measure topography as this mode has better force sensitivity, while several studies have demonstrated that the 2nd flexural mode can also provide similar topography measurement capability. In this study, considering the very tiny electrostrain and times higher effective stiffness of the 2nd flexural mode to optimize the sensitivity, the 1st flexural mode is employed to detect the electrostrain while the 2nd flexural mode, operated in a classic frequency modulation mode, is used for topography measurement. As the electrostrain and topography measurements are completed by two flexural modes independently, it seems that the same technique principle of PFM can be directly applied to this new system. However, as the QTF is a capacitor-like device without any electric shielding, a severe capacitance cross-talk will be induced in the QTF when AC drive is applied to the sample, causing a very strong background interference in the output of the QTF (S1, Supporting Information). If the conventional PFM’s homodyne detection is used here, the target electrostrain signal will be totally masked by this strong background interference, causing the demodulation of the electrostrain signal almost impossible. In addition, since there is no electric shielding, the QTF will also
be excited by the sample’s AC drive as well as the associated electrostatic force, which will introduce an apparent parasitic oscillation and then make the measured electrostrain signal largely ambiguous. Therefore, the classic homodyne detection scheme used in PFM cannot be transplanted to the QTF-based system to measure electrostrain. Recently, the invention of Heterodyne Megasonic PFM (HM-PFM) provides a different way to measure the electrostrain by using the heterodyne detection method.\textsuperscript{[66,67]} In HM-PFM, the frequencies of the target electrostrain signal and the sample’s AC drive are largely different, which tactfully makes the co-frequency interferences in conventional PFM, for example, the electrostatic force, can be minimized significantly. Based on this design, the above-mentioned co-frequency interferences in QTF system, including the capacitance cross-talk and parasitic oscillation, can also be avoided if a heterodyne detection scheme is adopted.

To achieve heterodyne detection for the dynamic electrostrain, another oscillation component should be provided as the reference, then the electrostrain and the reference oscillations can be mixed mechanically to obtain the difference-frequency component through the non-linear tip-sample interactions.\textsuperscript{[68]}

Combining Equations (1) and (2) and then ignoring all the static and high-frequency items, the difference-frequency force item of interest is:

\[ F_{\text{diff}} = -\frac{1}{2} A_s A_0 \cos(2\pi f_{\text{diff}} t + \phi_s - \phi_0) \]  

where \( f_{\text{diff}} = f_s - f_h \) is the difference frequency. The difference-frequency force \( F_{\text{diff}}(z) \) is the product of the mechanical frequency mixing process, which contains the electrostrain information of interest. It is obvious that any change of the amplitude \( A_0 \) and phase \( \phi_s \), such as \( A_0 \) decreasing at the ferroelectric domain wall and 180° \( \phi_s \) change between the oppositely polarized domains, will be reflected by the changes of \( F_{\text{diff}}(z) \). To detect this difference-frequency force by QTF, \( f_{\text{diff}} \) is intentionally set to be the resonance frequency of the 1\textsuperscript{st} flexural mode thus resonance enhancement can be used to obtain a better detection sensitivity and SNR. From Equation (3), it is clear that if the 2\textsuperscript{nd}-order force gradient \( F''_{ts}(z_0) \), the amplitude \( A_0 \) and phase \( \phi_s \) of the \( n \)\textsuperscript{th} flexural mode are constant, the amplitude and phase of the electrostrain vibration can be extracted from the motion of the 1\textsuperscript{st} flexural mode.

2.3. Experimental Set-Up

The model NC-HEsFM system is constructed on a commercial Scanning Probe Microscope (SPM) system (SPA400, Seiko Instruments, Japan). In order to use QTF as the force sensor for non-contact scanning, both the original height feedback circuit and the probe holder of the SPM system have been modified. The complete set-up of this model system is schematically shown in Figure 1A. A conductive AFM cantilever is glued at the end of the QTF prong using conductive silver paste (Figure 1B), and then the QTF sensor is mounted.
on a piezo transducer with a small dip angle (Figure 1C). The dip angle guarantees that the nano-tip on the cantilever end is located at the forefront of the sensor when engaging to the sample surface (Figure 1C). As the additional mass induced by the AFM cantilever and the silver paste is very small, the resonance of the QTF can still keep a high Q factor after the tip is attached. Figure 1D,E respectively show the typical free resonance curves of the 1st and 2nd flexural mode (anti-symmetric vibration) measured from the QTF with the AFM tip attached, in which a Q factor of \( \approx 4000–6000 \) (\( \approx 8000–10\,000 \)) in the 1st (2nd) flexural mode is usually obtained. Although both the 1st and 2nd flexural mode can be used for topography measurement,[63,64] in the model NC-HEsFM system, only the 2nd flexural mode is employed to measure topography while the 1st flexural mode is used to detect the DFE signal because of its higher sensitivity. In the NC-HEsFM designed here, the QTF electrode with the tip connected is set to be grounded while the drive signal for stimulating electrostrain is sent to the conductive substrate of the sample. During measurement, the QTF is mechanically excited to vibrate at its 2nd and a higher \( n^{\text{th}} \) (\( n \geq 3 \)) flexural mode (anti-symmetric vibration) simultaneously by the holder drive at frequency \( f_h \) and \( f_2 \) respectively, while the sample electrostrain is stimulated by the sample drive at frequency \( f_s \). To maximize the SNR of the DFE signal, the difference frequency \( f_{\text{diff}} \) is set to near the resonance frequency of the 1st flexural mode. The deflection signal which contains all the QTF vibration information is obtained by amplifying the QTF current through a current amplifier located close to the QTF. A phase-locked loop (PLL) or an internal signal source can be used to track the resonance frequency shift \( \Delta f_2 \) of the 2nd flexural mode, and the \( \Delta f_2 \) is used as the height feedback signal for constant frequency shift scanning. Typically, under the ambient conditions, the tip is much easier to work with a positive frequency shift setpoint \( \Delta f_{\text{sp}} \),[52,58,63] while in the high vacuum environment, a negative \( \Delta f_{\text{sp}} \) is usually used to achieve atomic resolution imaging.[50,54] As the effective Q factor of the QTF changes dramatically when the tip comes close to the sample, an automatic gain control (AGC) is designed here to keep the vibration amplitude of the 2nd flexural mode at a constant setpoint \( A_{\text{sp}} \). For the closed-loop feedback control, the classic proportion-integration (PI) strategy is adopted for both PLL and AGC. The DFE signal is demodulated by using a lock-in amplifier, in which the difference-frequency reference signal is produced by a home-made analog multiplier and a low-pass filter (LPF). Alternatively, the reference signal can be provided internally by synchronizing the clocks of signal source and lock-in amplifier.[36] The demodulation results, that is, the amplitude and phase of the DFE signal, are sent to the controller of SPM and then synchronously imaged with the topography (all the amplitude images here are shown in dimension of a.u.).
2.4. Ferroelectric Characterization

To test the model NC-HEsFM system, several typical ferroelectric materials, including periodically poled lithium niobate (PPLN) single crystal, Pb(Zn_{1/3}Nb_{2/3})O_3-9%PbTiO_3 (PZN-9%PT) single crystal, Pb(Zr,Ti)O_3 (PZT) film, and BiFeO_3 (BFO) film are selected here as the standard samples since the electrostrain contrasts (dominated by inverse piezoelectric effect) on those samples are deterministic and well defined in the literature. Figure 2A–C show the typical scanning results of the PPLN by NC-HEsFM. It is initially surprising that the simultaneously measured topography (Figure 2A) shows many particle-shaped fine structures on the PPLN surface (see more data in Figure S2, Supporting Information), which has been rarely revealed by conventional contact-mode PFM in the previous studies. These fine structures are likely the residuals from the microfabrication processes of the PPLN sample. NC-HEsFM is operated in a true non-contact mode, the surface damages or modifications have been eliminated thus the original surface status, including many details, can be well-preserved and then defined by the nano-tip. A detailed comparison between conventional PFM and NC-HEsFM with respect to the surface modification will be discussed later. From the amplitude and phase images of the DFE signal, the domain walls between the two adjacent domains can be clearly observed in the amplitude image (Figure 2B), and the periodical domains with alternative upward and downward polarization are distinctly revealed in the phase image (Figure 2C). Meanwhile, Figure 2B,C indicate an almost uniform amplitude distribution and a nearly 180° phase difference between the domains with opposite polarization, which agrees well with the characteristics of the proposed “ideal” ferroelectric characterizations. Another ferroelectric sample, PZN-9%PT single crystal, is also studied by NC-HEsFM. The PZN-9%PT sample tested here has...
spontaneously polarized domains in which the polarization is along the thickness direction, and the upward and downward domains are randomly distributed. Typical topography and simultaneously obtained electrostrain images of the PZN-95%PT sample are shown in Figure 2D–F. Clear labyrinthine domain pattern and ≈180° phase difference between the upward and downward domains can be observed, which are consistent with the reported results,

thereby once again confirming the validity of NC-HEsFM in ferroelectric domain characterization.

Similar to the conventional PFM, NC-HEsFM also allows to manipulate the ferroelectric domain by applying DC electric field. Figure 2G–I show the structure of an artificially written domain on PZT film. The circular domain is created by maintaining the tip at the near-surface (feedback on) while applying a -8 V DC voltage to sample (tip grounded) for ≈10 s, then this artificial domain is in situ imaged by NC-HEsFM. The clear domain contrast shown in Figure 2H.I indicates that NC-HEsFM can perform similar ferroelectric lithography as that in conventional PFM but in a non-contact manner. Another important observation is that the NC-HEsFM can theoretically break the sub-10 nanometers resolution limit of the conventional PFM, to demonstrate this, a high-resolution scanning (10×10 nm²), has been conducted around the domain wall area of the artificial domain (indicated by the white box of Figure 2H), and the results are displayed in Figure 2J–L. From the DFE amplitude (Figure 2K) and phase (Figure 2L) images, it can be seen that the position of zero amplitude and 180° phase jump are defined within a ≈2 nm range (indicated by the white dashed lines). Note that some thermal drift may exist between the amplitude and phase images, as they are sequentially acquired by performing in situ scanning twice (due to the limited signal channel of the SPA400 system). Theoretically, when the nano-tip is scanning over the narrow domain wall (estimated to be ≈1 nm wide), the amplitude and phase signal will correspondingly drop to zero and jump 180° respectively, implying that the zero amplitude and 180° phase jump can reflect the position of the domain wall. However, in conventional PFM, the piezoresponse signal usually has a considerable contribution from the local and distributed electrostatic force, causing the zero amplitude and 180° phase jump cannot reflect domain wall information accurately. In contrast, the electrostatic force, including both the local and distributed part, has been significantly minimized in NC-HEsFM (will be discussed later), thereby the observed ≈2 nm range of zero amplitude and 180° phase jump (Figure 2K,L) indicate that the domain wall position can be determined with a lateral resolution of ≈2 nm. To the best of our knowledge, such high-resolution domain wall images have hardly been reported previously by using the conventional PFM in the ambient environment. However, the results of Figure 2J–L do not reflect the resolution limit of NC-HEsFM as the current model system has quite strong thermal noise, thermal drift, and feedback noise (can be observed from the topography image, Figure 2J), and at the same time, the sample surface and tip, as well as the environmental conditions, do not well support high-resolution imaging in the current model system. According to the prediction by Kalinin et al., it is reasonable to expect that, under the conditions where atomic resolution imaging can be easily achieved by using QTF-based NC-AFM, NC-HEsFM may be able to provide an atomically resolved characterization for ferroelectric domain due to its superior capabilities of non-contact detection and electrostatic force minimization.

In addition, the measurement of ferroelectric hysteresis loop (switching spectroscopy) by using NC-HEsFM is also demonstrated here. The switching spectroscopy in NC-HEsFM is similar to that in the conventional PFM. A continuous or pulsed triangular wave-like DC bias sequence is superimposed on the AC drive and then applied to the sample to induce the polarization switching, while at the same time, measuring the DFE signal as a function of DC bias. Here, a continuous triangular DC probing wave with a step duration of 2 ms is employed to measure the hysteresis loop of the PZT film, which is similar to the macroscopic polarization-electric field hysteresis loop measurement.

Figure 2M displays the attained hysteresis loops of PZT film. The NC-HEsFM amplitude loop (top) and phase loop (middle) show the classic butterfly shape and dual 180° phase jumps respectively, which are the standard characteristics of ferroelectricity. Meanwhile, the DFE in-phase (bottom), calculated by [amplitude × cos(phase)], manifests the typical ferroelectric hysteresis with applied DC bias.

Intriguingly, the DFE phase loop shows a non-symmetric evolution trend where a ≈180° phase difference can be observed between two polarization switching points, which is quite different with the symmetric phase loop obtained by using the conventional PFM. This interesting non-symmetric phase evolution may indicate that the DFE phase signal can differentiate the two opposite polarization switching states, while the mechanism is pending for further investigation. Note that, instead of using the pulsed DC method to minimize the electrostatic force effect as that used in the conventional PFM, the continuous DC method is employed here to acquire hysteresis loops. The obtained results, however, does not show observable features of the electrostatic force effect, this improvement in fact benefits from the NC-HEsFM’s capability to suppress the electrostatic force and this will be discussed later.

Similar experiments, including both domain writing and switching spectroscopy, have been conducted on BFO film and the results are displayed in Figure S3, Supporting Information. In brief, the results shown in Figure 2 and Figure S3, Supporting Information, well demonstrate that NC-HEsFM can provide standard ferroelectric domain characterization, domain manipulation, and hysteresis loop measurement.

2.5. Multi-Eigenmode Operation

In addition, NC-HEsFM can be operated at multiple eigenmodes. As the QTF has theoretically an infinite number of flexural modes, all the flexural modes with mode number n ≥ 3 are supposed to be able to achieve the heterodyne detection of the electrostrain in NC-HEsFM if each eigenmode can be excited effectively. Therefore, in this work, six flexural modes (anti-symmetric vibration) with mode numbers from 3 to 8 are employed to measure the domain structure of the PPLN sample, and the results are displayed in Figure 3A,F, respectively. Finite element simulation (see simulation details in S7, Supporting Information) is implemented to obtain the mode shape (images in the first row of Figure 3) and eigenfrequency of each mode, and the experimentally determined eigenfrequencies agree well.
with the simulation results (Table S1, Supporting Information). From Figure 3, it is obvious that all of the six flexural modes can be used for electrostrain measurement, and the results, including DFE amplitude and phase images, attained using each flexural mode manifest almost the same contrast of the domains. Note that nonuniform distribution of DFE amplitude can be observed on several amplitude images (Figure 3A,E,F), this is most likely caused by a background difference-frequency interference as it is found that there is a difference-frequency component generated in the current amplifier due to its non-linear effect (S2, Supporting Information). By applying appropriate modifications to the original current amplifying circuit, such as adding LPFs, the difference-frequency component can be minimized. The operability of multiple eigenmodes implies that, when necessary, the excitation frequency can be adjusted via mode selection. For instance, when using NC-HEsFM to measure electrochemical Vegard strain, the 3rd flexural mode may be used to obtain a stronger signal as a lower excitation frequency corresponds to a larger Vegard strain.\[^{[38]}\] Whereas if the sample under test is prone to be affected by electrochemical Vegard strain or dynamic electrochemical reactions, the 8th or even higher flexural mode can be used since higher excitation frequency can help to minimize these influences.\[^{[21,66,67]}\]

### 2.6. Non-Destructive Characterization

Generally speaking, it is believed that the conventional contact-mode PFM is a non-destructive method for nanoscale piezo/ferro-electric characterization.\[^{[19,82]}\] However, the contact-mode PFM scanning can be extremely prone to introduce modifications to both the sample surface and tip apex due to the relatively large and continuous tip-sample repulsive interaction, indicating that it is very difficult to maintain a constant tip and sample status during the entire PFM scanning process. Therefore, the contact-mode operation of the conventional PFM usually causes a lot of challenges to the reproducibility of the final topography and PFM images. Herein, the as-purchased fresh PPLN sample has been used to demonstrate the destructive yet irreversible scanning of the conventional PFM. PPLN is a standard sample which has been used to calibrate the PFM signal, and many PFM images of PPLN including the simultaneously obtained topographies have been reported.\[^{[66,70]}\] Similar results can also be obtained in our experiments when performing the conventional PFM measurements (S3, Supporting Information). However, when PPLN is measured by the newly developed NC-HEsFM, it is surprising at the beginning to see so many fine structures on the surface (Figure 2A), which has seldom been revealed previously by PFM on commercial PPLN samples.\[^{[66,70]}\] A detailed investigation of the reason has been conducted by performing in situ tapping-mode AFM and PFM scanning on PPLN, and the results clearly reveal that the large topography difference between the conventional PFM and NC-HEsFM measurements is caused by the destructive scanning of the conventional PFM (S4, Supposing Information). Since the NC-HEsFM uses a non-contact manner to detect the electrostrain, the scanning processes are non-destructive and stable. Figure 4 shows a typical in situ zoom-in scan

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**Figure 3.** NC-HEsFM ferroelectric characterization with different eigenmodes. A–F) In situ NC-HEsFM measurement results of PPLN sample by using the 3rd to the 8th flexural mode of the QTF, respectively. The 1st raw to 4th raw respectively show the finite element simulated mode shapes, topography images, DFE amplitude and DFE phase images. Measurement conditions: (A) \(f_h = 522.508\) kHz, \(f_s = 555.107\) kHz; (B) \(f_h = 953.954\) kHz, \(f_s = 986.533\) kHz; (C) \(f_h = 1459.566\) kHz, \(f_s = 1492.165\) kHz; (D) \(f_h = 2015.098\) kHz, \(f_s = 2047.697\) kHz; (E) \(f_h = 2594.125\) kHz, \(f_s = 2626.724\) kHz; (F) \(f_h = 3195.517\) kHz, \(f_s = 3228.116\) kHz; \(f_{\text{diff}} = 32.599\) kHz, \(\Delta f_{\text{sp}} = +25\) Hz, \(A_{\text{sp}} = 10\) mV. Scale bar in (A–F) is 3 \(\mu\)m.
implemented by the NC-HEsFM. The initial scanning results are shown in Figure 4A,B, in which the original fine structures have been well defined in the topography images and no noticeable changes can be observed between the first (Figure 4A) and second (Figure 4B) scanning. Continuous zoom-in scanning has been conducted in situ to check if any modifications emerge and the results are shown in Figure 4C–G. Figure 4C–F show the obtained topography images corresponding to the scanning areas indicated in Figure 4B,D respectively. Clearly, no indications of the surface modification can be observed during the continuous non-contact scanning. To verify that the fine structures on PPLN surface can be easily damaged, a very weak indentation has been applied by the tip at the point shown in Figure 4F. Figure 4G shows the topography image obtained after the indentation experiment. A triangular pyramid indentation can be clearly observed (Figure 4G), implying that this surface layer indeed has a weak mechanical strength and that’s why it can be easily damaged by the contact-mode scanning (Figure S6, Supporting Information). After many times zoom-in scans, a final scan has been performed within the initial area to check the surface status and the result is displayed in Figure 4H. Comparing Figure 4A,B with 4H, nearly no zoom-in scanning traces and surface modifications can be observed, which indicates that the NC-HEsFM has achieved a real non-destructive measurement. The PPLN surface area with large protrusion structures has also been imaged to test the non-destructive measurement of the NC-HEsFM, and the results are presented in Figure S7, Supporting Information. Meanwhile, a much stricter and longer experiment which includes 16 times in situ scanning (last for ≈9 h) has been conducted to test the stability and reproducibility of NC-HEsFM (S5, Supporting Information). All the results clearly demonstrate that the NC-HEsFM can stably provide a non-contact, non-destructive and reproducible manner for simultaneous topography and electrostrain measurement. Since both the tip and sample surface can be largely protected in the NC-HEsFM measurements, the initial tip and sample status, especially for the atomically sharp tip and atomically flat surface, now can be well kept during the scanning, which provides ideal conditions for achieving ultrahigh-resolution imaging.[4,7] However, such ultrahigh-resolution imaging usually requires strict measurement conditions or environments, typically high vacuum or even low temperature, and moving the NC-HEsFM system to a vacuum chamber needs many modifications thus this part of the study will be revealed in the future.

2.7. Electrostatic Force Effect

Electrostatic force is known as a great yet long-standing challenge for conventional PFM. As discussed earlier, huge efforts have been made to address this intractable problem, however, the proposed solutions are still subject to many limitations due to the technique principle of the PFM. The invention of HM-PFM breaks the conventional technique frame and provides a brand-new pathway to minimize the electrostatic force by using heterodyne detection and high-frequency excitation. The mechanism of minimizing the electrostatic force effect in HM-PFM has been systematically discussed in our previous study,[66] and in brief, it is based on two aspects, one is the significantly increased effective stiffness of the cantilever at high eigenmodes, and another is the heterodyne detection which breaks the direct coupling between the electrostrain and electrostatic force signals. In NC-HEsFM, the 1st flexural mode of the QTF has a stiffness as high as ≈1800 N m⁻¹,[50,62] which is already far larger than that of any conventional cantilever, let
alone the $n^{th}$ ($n \geq 3$) flexural mode where the effective stiffness increases sharply with the mode number $n$. Therefore, during NC-HESFM measurement, the QTF will certainly have a large enough stiffness to minimize both the local and distributed electrostatic force effects. Meanwhile, the heterodyne detection scheme has also been used in the NC-HESFM, thus with the basis of HM-PFM, NC-HESFM should achieve a similar or even much better of electrostatic force minimization. To confirm this capability, the widely used electrostatic force examining method, that is, the DC spectroscopy, is conducted on PPLN by using conventional PFM and NC-HESFM. Figure 5A,B show the PFM amplitude and phase as a function of DC bias, respectively. In Figure 5A,B, the typical electrostatic force-induced V-shaped amplitude curve and $\approx 180^\circ$ phase change can be observed clearly, implying that the electrostatic force is significantly affecting the PFM signal. In contrast, completely different variation trends of the DFE amplitude and phase can be observed in the measurement of NC-HESFM (Figure 5C,D). It is evident that, even though a large DC bias scanning range ($\pm 30$ V) is used, all of the DFE amplitude and phase signals measured by six different flexural modes can keep a constant magnitude with changing DC bias, which unambiguously indicates that the electrostatic force effect, including both the local and distributed part, has almost been completely eliminated in the NC-HESFM. With this superior capability of minimizing electrostatic force effect, the domain wall position can thereby be determined accurately from the DFE amplitude and phase images (Figure 2K,L) and at the same time, a standard ferroelectric hysteresis loop (Figure 2M) can be obtained even though continuous DC method is used in the switching spectroscopy measurement.

2.8. Mechanism of Effective Electrostrain Measurement

Above results clearly show that NC-HESFM can effectively detect the tiny electrostrain in a true non-contact manner. Therefore, an obvious question is why NC-HESFM can achieve the effective electrostrain measurement while the intermittent-contact mode PFM cannot. As discussed in the previous section, the key factor is about the tip-sample distance because it dominates the electric field distribution and tip-sample interaction force. To show how tip-sample distance ($z$) affects the electric field distribution, a finite element simulation has been performed to calculate the electric field distributions under different $z$, and the results are shown in Figure 6A,B (see simulation details in S7, Supporting Information). Figure 6A,B show the cross-sectional and surface electric field distributions with $z = 0.1, 2.1, 4.1$ nm, respectively. Meanwhile, the line profiles (indicated in Figure 6B) of the surface electric field strength under a series of values of $z$ are plotted in Figure 6C. From Figure 6A–C, it is obvious that the effective electric field applied to the sample dramatically decays with increasing tip-sample separation even though the tip is only lifted by a few nanometers. Therefore,
when using a conventional cantilever-based tip to measure electrostrain with non-contact or intermittent-contact mode, the large tip vibration (typically with amplitude of a few to tens of nanometers) can hardly stimulate a relatively stable and large enough surface strain. In addition to the electric field, the tip-sample interaction is also of great importance for effectively detecting the electrostrain since the tiny surface strain is measured indirectly based on a strong enough tip-sample interaction. Here, for simplicity, the well-studied Si-Si (Si tip on Si surface) interaction model has been employed to demonstrate the relationship between tip-sample interaction force and $z$. Figure 6D shows the calculated 1st-order force gradient as a function of $z$ for ideal tip-sample (Si tip on Si surface) interaction. Here, for simplicity, the well-studied Si-Si (Si tip on Si surface) interaction model has been employed to demonstrate the relationship between tip-sample interaction force and $z$. Figure 6D shows the calculated 1st-order force gradient as a function of $z$ for ideal tip-sample interaction.

Figure 6D shows the calculated 1st-order force gradient as a function of $z$ under the assumption of ideal tip and surface (the calculation details in S6, Supporting Information). Since the tip-sample force gradient determines the coupling between the sample surface and tip when measuring electrostrain, such a sharp attenuation trend of the force gradient shown in Figure 6D clearly indicates that even lifting the tip by $\approx 1 \text{ nm}$, the force gradient thereby the sensitivity for surface displacement can decrease dramatically. Therefore, using a cantilever-based tip to realize non-contact or intermittent-contact detection of electrostrain is very challenging. From Figure 6A–D, it can be found that if the dynamic tip-sample separation is well controlled within the range of angstrom, there should be a large possibility to achieve effective electrostrain measurement, and in fact, this is the main mechanism used in NC-HEsFM. To confirm this, the practical tip vibration amplitude of NC-HEsFM has been estimated using the thermal noise analysis method. Figure 6E,F show the typical power spectral density (PSD) spectrums of the output voltage noise (from current amplifier) acquired around the eigenfrequency of the 1st and the 2nd flexural mode, respectively. By defining a voltage deflection sensitivity $\alpha$, the voltage noise PSD of an eigenmode can be expressed as (see details in S8, Supporting Information):

$$S_{vv}(f) = \frac{4k_B T f_0^2}{(f_0^2 - f^2)^2} + \left(\frac{f_0 f}{Q}\right)^2$$  \hspace{1cm} (4)$$

where $k_B$, $T$, $f_0$, and $k_0$ are Boltzmann constant, temperature, resonance frequency, and mode stiffness, respectively. By fitting the PSD spectrums of the two modes using Equation (4) and the constants of $T = 298.15 \text{ K}$, $k_0 = 1800$ (1st flexural mode), and $70 740 \text{ N m}^{-1}$ (2nd flexural mode), the voltage deflection sensitivity of the 1st and the 2nd flexural mode can be obtained, which are 21 and 62 $\mu \text{V pm}^{-1}$ (for two-arm anti-symmetric vibration), respectively. With the deflection sensitivity, the tip vibration amplitudes of the NC-HEsFM can be estimated to be $\approx 30–160 \text{ pm}$ (2nd flexural mode) and $\approx 20–40 \text{ pm}$ (1st flexural mode) in this study. For the $n^{th}$ high flexural mode, the vibration...
amplitude cannot be estimated by this thermal noise method as its PSD spectrum manifests below the noise floor. However, the amplitude of the $n$th flexural mode should be close to or even smaller than that of the 2nd flexural mode since, during the normal NC-HEsFM measurement, no change can be observed in both PLL and AGC feedbacks when the high mode drive is turned on/off. Using the operation condition of $\Delta f_p = \pm 20 \pm 50$ Hz, the average force gradient during a vibration period can be estimated to be $\approx 14$–36 N m$^{-1}$ (under small amplitude approximation).\cite{50} According to the estimated amplitudes and average force gradient, it can be concluded that, during the whole vibration period, the tip-sample distance in NC-HEsFM can be well controlled within angstrom or even sub-angstrom range, which can guarantee the strength of both electric fields in the sample and tip-sample interaction thus effective electrostrain measurement can be achieved in NC-HEsFM.

3. Conclusion and Outlook

In this study, an advanced scanning probe technique called NC-HEsFM has been introduced, to measure the nanoscale electrostrain in a true non-contact manner. By using QTF force sensor and heterodyne detection scheme, NC-HEsFM achieves the goal of non-contact ferroelectric characterization at nanoscale. It has been demonstrated that NC-HEsFM can perform ideal high-resolution ferroelectric domain mapping, standard ferroelectric hysteresis loop measurement, and controllable domain manipulation by using multiple eigenmodes. Comparing with the conventional PFM measurements, NC-HEsFM shows a superior capability in achieving real non-destructive ferroelectric characterization with significantly minimized local and distributed electrostatic force effects. The qualitative analysis based on theoretical model and finite element simulations indicates that the effective electrostrain measurement achieved in NC-HEsFM stems from the highly controllable angstrom or even sub-angstrom tip-sample separation offered by the QTF sensor. In brief, NC-HEsFM has simultaneously overcome the most fundamental and long-standing issues such as contact-mode operation, resonance tracking, and electrostatic force faced by conventional PFM, providing a significantly improved, non-contact yet non-destructive, automatically resonance tracked and electrostatic force minimized way for nanoscale ferroelectric or piezoelectric studies.

In addition, the small volume and piezoelectric self-detection of the QTF sensor make NC-HEsFM an ideal candidate for measuring nanoscale electrostrain under extreme environments like vacuum and low temperature, which can support the studies towards elucidating those most fundamental ferro/piezoelectric physics, such as the ferroelectric polarization dynamics.\cite{8} Given the ultra-high spatial resolution achieved in the QTF-based NC-AFM, it is believed that, under the proper conditions like vacuum, NC-HEsFM may provide similar high-resolution imaging for electrostrain measurement. Furthermore, the ultra-stiff QTF prong enables NC-HEsFM to perform in situ STM or tunneling spectroscopy measurements, which can be of great meaning for studying the ferro/piezoelectricity of ultrathin films\cite{61,85} and conductive ferroelectric domain walls.\cite{86} In addition, NC-HEsFM can be simply modified to measure the high-order electrostrains (S9, Supporting Information),\cite{36} such as the 2nd-order electrostrictive strain,\cite{41} in which the contact-mode and the 2nd-harmonic electrostatic force issues are expected to be avoided comparing to that of the currently-used PFM-based method.\cite{41} Finally, the success of the NC-HEsFM can be easily transplanted to multiple other surface strain-based SPM\cite{46} such as the ultrasonic strain-based Atomic Force Acoustic Microscopy,\cite{87} the photothermal strain-based Infrared-AFM or photothermal induced resonance technique,\cite{88} the magnetomechanical strain-based Piezomagnetic Force Microscopy\cite{89} and the Joule thermal strain-based Scanning Joule Expansion Microscopy,\cite{90} which will bring significantly improved characterization capabilities for studying the nanoscale surface strains, as well as the corresponding physical properties, under the excitation of electric, acoustic, optical, magnetic and temperature fields.\cite{36}

4. Experimental Section

Experimental Set-up: The model NC-HEsFM system was established on a commercial SPM (SPA400, Seiko Instruments), and hardware modifications were implemented to enable external height feedback control. The original tip holder was redesigned for the application of QTF sensor. The AC excitation signals were generated by an arbitrary waveform generator (Keysight 335228, Keysight Technologies). An embedded field-programmable gate array (FPGA) controller (NI cRIO-9064, National Instruments) equipped with one digital acquisition card (NI 9775, National Instruments) and one analog output card (NI 9263, National Instruments) was utilized to complete the signal acquisition, PLL, and AGC feedback control. A current amplifier (DLPCA-200, FEMTO) with the gain of $1 \times 10^5$ V A$^{-1}$ was employed to amplify the QTF current signal. The demodulation of the AC signals was finished by using a multi-channel lock-in amplifier (MFLI, Zurich Instruments). The home-made functional circuits, including analog multiplier, low pass filter, and summing amplifier, were used to complete AC signal summation and AGC amplitude control as well as generate the difference-frequency reference signal. DC bias was provided by a digital source meter (Keithley 2450, Tektronix), and the superposition of DC bias to AC drive was finished by a bias-tee. All the programmable instruments were controlled by the self-developed NC-HEsFM control program based on LabVIEW and LabVIEW FPGA (National Instruments).

SPM Characterization: A QTF (Type E158, Micro Crystal) with fundamental resonance frequency of 32.768 kHz was used in this study as the force sensor.\cite{36} A PtIr5 coated conductive AFM probe (PPP-NCSTPt, Nanosensors) was employed here as the scanning tip, of which the cantilever was glued at the end of the QTF prong using conductive silver paste. When the AFM tip was disabled, it can be simply removed from the QTF with the aid of organic solvent and a new tip can be mounted again.\cite{36} During the scanning, the scanning line speed was $0.25$–$0.75$ lines s$^{-1}$, and to keep the tip operated in a non-contact manner, the frequency shift setpoint for height feedback control and the amplitude setpoint of the AGC were typically set to $\approx 20$–$50$ Hz and $\approx 2$–$10$ mV (estimated to be $\approx 30$–$160$ pm), respectively. A typical frequency shift-distance curve is shown in Figure S11, Supporting Information. Due to the limited signal acquisition channel of the SPA400 system, the amplitude and phase images of NC-HEsFM were sequentially acquired by executing in situ scanning twice. The drive amplitudes for the higher flexural mode and sample were typically set to $\approx 0.05$–$10$ V$_{pp}$ and $\approx 2$–$8$ V$_{pp}$ respectively. For the conventional PFM measurement, a Pt coated conductive AFM probe (240AC-PP, OPUS) with a force constant of $\approx 2$ N m$^{-1}$ and free resonance frequency of $\approx 70$ kHz was used. All measurements were conducted in an ambient environment with tip grounded. Although this study was conducted in an ambient environment due to the limitation of SPA400 system, it was highly recommended to perform NC-HEsFM measurements, especially
the ferroelectric domain manipulation and hysteresis loop measurement, in noble gas atmosphere or vacuum because it was found that these measurements were prone to induce surface electrochemical reactions under ambient conditions.\(^{[3]}\)

**Sample Preparation:** A commercially available PPLN standard sample (AR-PPLN test sample, Asylum Research, Oxford Instruments) was used, which consists of a 3 mm × 3 mm transparent die with a thickness of 0.5 mm. The PZT-9%PT single crystal (supplied by Microfine Materials Technology Pte. Ltd., Singapore) was cut into small pieces with a rectangular shape and the respective orientations are [001]/[010]/[001] and the surface of the samples was polished with SiC papers and alumina powder using water-cooled polisher. After the polishing processes, the dimension of the samples was approximately 4 mm (width) × 4 mm (length) × 0.5 mm (thickness). The PZT 20/80 film with a thickness of ~300 nm was grown in SrRuO\(_3\)-buffered SrTiO\(_3\) (STO) substrate with (001) orientation using pulsed laser deposition (PLD) (KrF excimer laser, \(\lambda = 248\) nm). The SrRuO\(_3\) layer (=50 nm) was first deposited on the STO substrate at a temperature of 680°C and an oxygen pressure of 15 Pa. Then the PZT layer was grown on top of the SrRuO\(_3\) layer at a temperature of 600°C and the same 15 Pa oxygen pressure. After growth, the film was cooled to room temperature at 10°C min\(^{-1}\) in an oxygen atmosphere of 1 atm. For the preparation of BFO(100nm)/LSMO(200nm)/STO film, a commercial 10% Bi excess BFO target was used to compensate for the Bi volatilization during the PLD growth process. The commercial La\(_{0.33}\)Sr\(_{0.67}\)MnO\(_3\) target was used to grow the LSMO layer. The BFO/LSMO heterostructure was grown on an STO substrate with (001) orientation using PLD at 700°C.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that supports the findings of this study are available in the supplementary material of this article.

**Keywords**

electrostrain, ferroelectric, non-contact ferroelectric characterization, piezoelectric, piezoresponse force microscopy, quartz tuning fork

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