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Local Characterization of Piezo-Responsive Materials

by Kenneth E Strawhecker and Latha Nataraj

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This study created two methodologies for local piezoresponse measurements of piezo-responsive materials using an atomic force microscopy: single-frequency piezoresponse force microscopy (PFM) and dual-AC resonance tracking-PFM. The methodologies were created to determine whether they were capable of 1) detecting and quantifying a piezoresponse and 2) comparing the quantitative piezoresponse of different materials. Five different probes and two different materials were used in this study.

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Summary

This study created two methodologies for local piezoresponse measurements of piezo-responsive materials using an atomic force microscope: single-frequency piezoresponse force microscopy (PFM) and dual-AC resonance tracking (DART)-PFM. The methodologies were created to determine whether they were capable of 1) detecting and quantifying a piezoresponse and 2) comparing the quantitative piezoresponse of different materials. Five different probes and two different materials were used in this study.

This study showed that single-frequency PFM is not an appropriate measurement methodology for studying the materials selected. It was apparent that the signal-to-noise ratio and sources of error were poor enough that it was not possible to quantifiably detect a piezoresponse from these materials. On the other hand, DART-PFM was shown to be capable of qualitatively and quantitatively measuring the piezoresponse of the materials compared. The benefit of this latter methodology was that the response signal was quantitatively larger than the noise. One drawback of DART-PFM was that after fitting to the SHO model, some part of the data was lost due to poor fitting. Another drawback was that through five probes used, three of them indicated the US Army Combat Capabilities Development Command Army Research Laboratory sample had larger d33, whereas the other two indicated the commercial sample had larger d33. Therefore, we suggest a more careful case study to further develop the DART-PFM methodology.

1. Introduction

Because of increasing interest in lead-free piezoceramics, new approaches to processing have been developed. These new approaches have led to several possible alternatives to conventional lead zirconate titanate (PZT) materials, such as potassium sodium niobate (K, Na) NbO_3, also known as KNN.[1–3] The synthesis of these new materials requires a fast-testing technique that can be performed on small quantities to reliably assess their potential performance enhancements for piezoelectric strain properties. For many years, the US Army has supported the development of lead-free technologies that satisfy environmental regulations associated with lead contamination. Since any use of lead pollutes the environment in small amounts, the more lead you remove from technology, the better it is for the environment.[4] For this reason, we have synthesized a variant of one of the most promising lead-free, nontoxic, environmentally friendly, and biocompatible piezoelectric material, named W-KNN, for a variety of applications in pressure sensors, actuators, energy harvesters, munitions and triggers, sonars, accelerometers, and medical prosthetics.[2] To support the characterization of such synthesized materials, we have developed nanoscopic electromechanical techniques under the category of atomic force microscopy (AFM)—specifically, piezoresponse force microscopy (PFM).

The PFM is an AFM mode that simultaneously probes electromechanical properties of a material at micro- to nano-length scales along with the material surface topography. Piezoelectric materials, and particularly their crystalline structures, may generate strain in response to an applied electric field or bias. The field may be direct current (DC) or alternating current (AC), and the material dimensional change response would track with the field over time. The amount of material strain response is defined as d33, the converse piezoelectric coefficient (or the piezoelectric strain constant), which is equal to the material dimensional change induced by the application of the electric field. The units of d33 are chosen as defined by the experiment. In this case (the "large signal," or "converse" piezoelectric coefficient), typical units are inverse piezoelectric coefficient (pm/V) and typical PZT material values are 200–500 pm/V, or on the order of 10^1–10^3.[5]

The PFM uses a conductive probe tip to apply a local electric field to a surface, causing deformation of piezo-responsive crystals at or near the surface. As the crystals expand or contract, a deflection of the cantilever occurs, allowing a mechanical response to be measured on the order of 1–100 pm/V. High-frequency measurements can be made where an AC bias is applied to the probe tip, and cantilever deflection is measured through a lock-in amplifier set to the bias frequency.[6] Dual-AC resonance tracking (DART, or DART-PFM) is a specific

PFM technique which ensures that the signal being measured remains at the tip-sample resonance frequency. This provides a natural means of amplifying the piezoresponse signal. Due to the amplified response on resonance, the amplitude (AMP) signal captured is fit to a simple harmonic oscillator (SHO) model to calculate the actual AMP response of the crystal to the applied bias.[6] In a simpler analysis, an off-resonance frequency can be selected (no "dual-AC/DART," but the single-frequency PFM [SF-PFM]), and the AMP signal is assumed to be the AMP response of the crystal to the same applied bias.[6] Due to the small AMP signal (order of picometers) and relatively large noise (vibration, electrostatic forces, or charging and capacitive issues), it is often very difficult to collect large enough signal-to-noise ratios such that reliable d33 values can be measured.

In this work, both methods are developed and applied to piezo-responsive materials. The results are used to compare techniques as well as results regarding novel KNN crystals purchased commercially and KNN-crystals synthesized at US Army Combat Capabilities Development Command (DEVCOM) Army Research Laboratory (ARL).[2] The resulting methodology is a practical technique that can be used to assess the local effective d33 material property of piezo-responsive materials such as these novel KNN crystals.

2. Methods, Assumptions, and Procedures

For DART-PFM, the PFM is used to probe the response of crystalline nanodomains by selecting regions at the sample surface and imaging at varied AC bias voltages while using the DART technique to enhance the PFM signal. The PFM signal is an AMP response by the probe on the crystalline surface. This is caused by the change in dimension of the crystal with AC bias and measured by the photodetector where a lock-in amplifier selects only the signal AMP that is in phase with the applied AC bias frequency. The basic experimental procedure is to engage the surface with the metal-coated probe (AC240 TM-R3, Asylum Research) with a force setpoint of approximately 65–85 nN (nominal optical lever sensitivity was 109 nm/V, spring constant was 0.3–4.8 N/m but typically approximately 1.4 N/m, and setpoint in volts was set to 0.5 V).

A PFM tune was performed to determine the tip-piezo response resonance peak frequency and phase. The frequency was typically between 250 and 300 kHz, and "high" and "low" frequencies were selected to envelope the resonance. These frequencies were selected to be at the high and low frequency roll-off values of the resonance peak so that their corresponding AMPs (amp1 and amp2 for the low and high frequency, respectively) were low relative to the resonance AMP. After data capture, amp1 and amp2 signals are fed to the SHO model in the vendor software to result in the corrected PFM AMP signal. Amp1 and amp2 were typically 5%–20% of the resonance AMP. Scans were performed at variable tip-sample bias value, or “drive AMP.” The drive AMPs were 5, 4, 3, 2, and 1V, respectively, for each of five scans, with 2- × 2-µm areas. Occasionally, 0V scans were performed and always resulted in simply the noise floor images for amp1 and amp2. To obtain the d33 values for each sample, amp1 and amp2 images were collected, and the values were fitted using Asylum Research software (version AR 16.10.211) to determine the actual tip AMP while in contact with the sample.

This SHO fitting by the vendor software resulted in a data channel Ao, which was treated as crystalline piezoresponse for the material at the given bias voltage. Using Gwyddion[*] the Ao image pixel values were returned in strain length (picometer), and image thresholds were used to quantify the d33 response by plotting thresholded Ao (selecting upper percentiles at 50th, 75th, 90th, 95th, and 99th percentile) as a function of bias voltage and quantifying the slope at each voltage (i.e., the ratio of strain length/bias voltage). Ao, and therefore d33 values, would be affected by things such as domain size, domain orientation, and characteristic deviation of material d33 strength from domain to domain. In addition, the threshold values are not averages, but they provide a way to quantify the response of well-oriented crystals versus either nonoriented crystals or pixels within the image that represent poor fitting in the SHO model and therefore are labeled “not a number.” Thus, the d33 values obtained can be referred to as “effective” d33, as noted in Gao[5] (p. 58). In summary, thresholding provides a way to quantify the response of only the most well-oriented crystal grains within the imaged area while eliminating noise in the acquired data.

For comparison, the technique developed above was repeated for the off-resonance frequency case (SF-PFM) for each self-same probe tip used in the DART-PFM analysis. The AMP signal collected was presumed to reflect the AMP response of the crystals to the applied bias voltage. No SHO fitting is required for SF-PFM. The same evaluation of best-case d33 value was performed and included thresholding to the same percentiles for comparison. Therefore, the difference between the two SF-PFM/DART-PFM experiments was as follows: 1) the sample surface locations were selected at random, and therefore the crystals were not necessarily the self-same crystals; 2) the tip was used first for DART-PFM and then for SF-PFM and thus could show effects of being worn (such as larger contact area); and 3) DART-PFM analysis must rely on SHO fitting to produce AMP response, whereas the off-resonance SF-PFM technique produces true AMP response.

[*] Gwyddion, version 2.66. http://gwyddion.net/

3. Results and Discussion

Since the SF-PFM is simple but not as useful in the present materials, those results will be reported first. Next, results from the DART-PFM technique will be presented. Finally, the Discussions section will include advantages and disadvantages of the techniques, assessments of the materials, and an overall discussion of the methodology.

3.1 Single-Frequency PFM

In SF-PFM, the tip is placed on the sample at a nominal contact mode force setpoint and frequency is swept through a range to see the AMP response. An off-resonance frequency is selected as the drive frequency for the AC bias. Any frequency that does not result in a peak may be selected; avoid natural electronics frequencies such as 60 Hz. For this experiment, 50 kHz was selected for AC bias frequency. The sample is then scanned in contact mode with the AC bias set to a particular voltage. Figure 1A and B shows the resulting topography images for the samples studied (ARL and commercial samples). Simultaneously, the AMP response over the scan area is recorded. For piezo-responsive materials, the applied AC bias should cause a height change to be measured, which, by using a lock-in amplifier in the AFM controller, will be recorded as an AMP signal, as shown in Fig. 1C and D for the ARL and commercial samples, respectively. This AMP signal is the PFM AMP response to a 1V-applied AC bias.

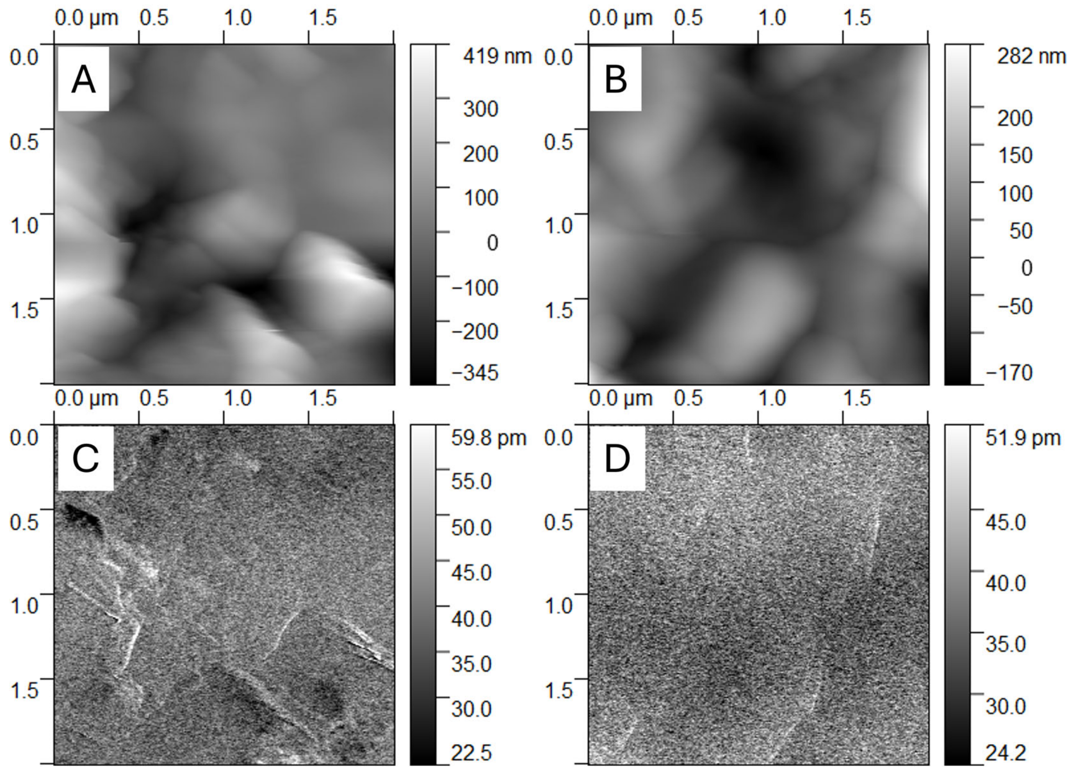

Fig. 1 Example of ARL and commercial sample height images (A and B, respectively) and corresponding AMP images (C and D, respectively) from SF-PFM at 1V-applied bias (original tip [tipO])

As seen in Fig. 1, the AMPs recorded range from 20 to 60 pm. This AMP is comparable to the noise floor, which is an image captured with 0.0V-applied AC bias, and typically has a range from 20 to 60 pm. Therefore, the signal at 1.0V-applied AC bias may not be a result of the piezo-responsive behavior of the materials. To assess this further, the AMP images from each bias voltage setting (1, 2, 3, 4, and 5V) were imported to EXCEL, and the AMP from each pixel was ranked so that the 50th, 75th, 90th, 95th, and 99th percentile levels could be measured. This is shown in the bar graphs in Fig. 2A and B for the ARL and commercial samples, respectively, using tipO. Careful inspection of these data shows that the 1 and 2V bias levels do not appreciably change the AMP signal for the ARL sample, and the same is true for the commercial sample up to 3V. At higher bias voltages (3–5V for ARL samples, 4 and 5V for commercial samples), it is possible to see appreciable and quantitative change in the AMP signals at these threshold percentages, where the AMP signal increases with bias voltage (for this particular probe, tipO). However, the effective d33 for the ARL and commercial samples at these bias voltages (Fig. 2C and D, respectively) appears to be decreasing across the full bias range studied for both series.

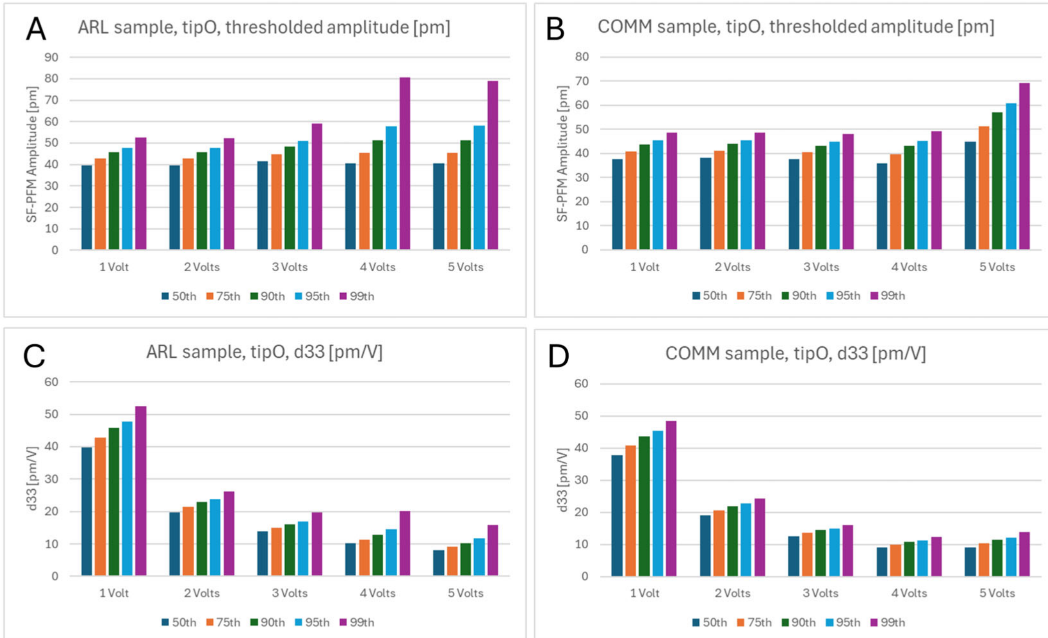

Fig. 2 **(A and B) Amplitude thresholds (50th, 75th, 90th, 95th, and 99th percentile) from SF-PFM at all applied bias values (ARL sample and commercial sample; tipO). (C and D) Corresponding d33 values, by taking the ratio of AMP/applied bias voltage (ARL sample and commercial sample; tipO).**

To compare probe tips and thereby ensure that this behavior is not caused by a faulty probe, this procedure was repeated for other similar probes. The results were similar to what was found using tipO. For every probe, there was little increase in AMP; wherever a small increase was seen, it was slightly more prominent for the ARL sample than the commercial sample. The effective d33 value always decreased with bias voltage. This behavior suggests that 1) the error in the measurements is large compared with the actual piezoresponse signal or 2) other contributing factors such as electrostatic interactions may be dominating the results.

3.2 DART-PFM

To sort out the actual piezoresponse of the ARL and commercial materials, we applied a dual-frequency approach to the materials. Figure 3 shows the height image (Fig. 3A) and the Ao image (Fig. 3B), illustrating the piezoresponse AMP (here at 1V). This is derived by inputting the A1 and A2 images (Fig. 3C and D, AMPs from near resonance) into the SHO model in the vendor software. Figure 4 shows the same images (Fig. 4A, height; Fig. 4B, Ao; Fig. 4C, A1; and Fig. 4D, A2) as those in Fig. 3, except for the commercial sample, again at 1V-applied AC bias. The "red" pixels in these images are "not a number," as determined by the SHO fit, and are ignored in the analysis.

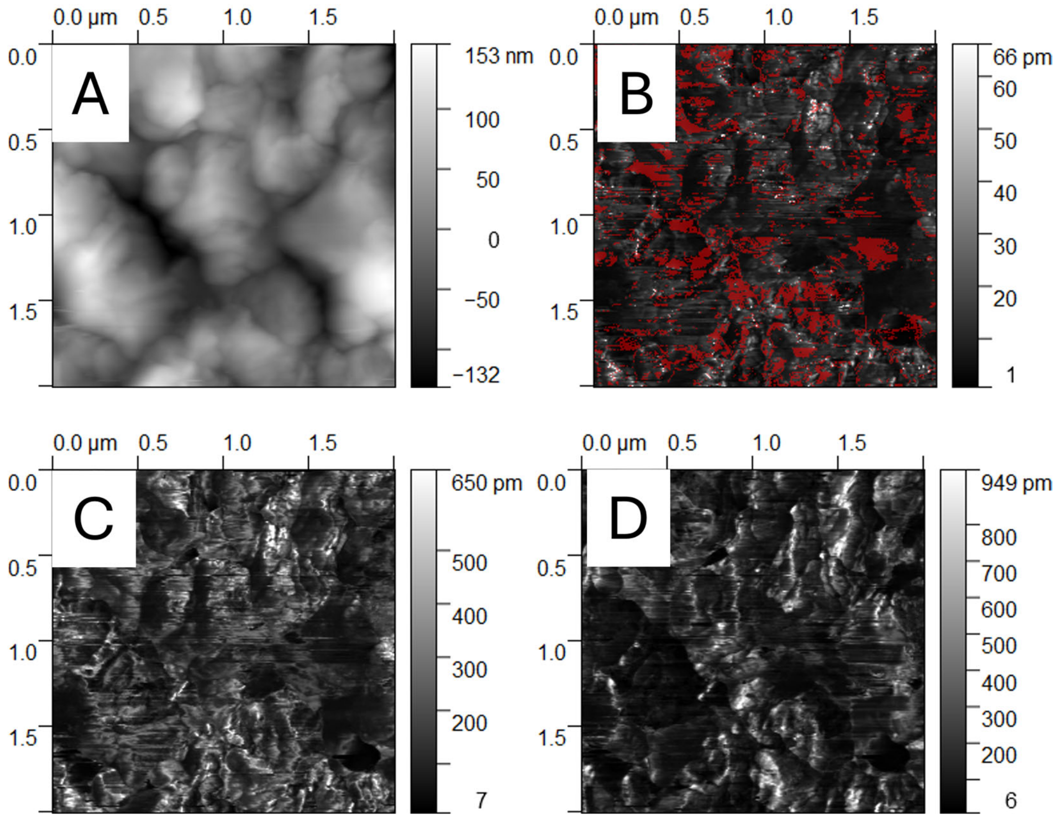

Fig. 3 **ARL height image (A) from DART-PFM using 1V-applied bias and the corresponding Ao image from the SHO model (B) using A1 and A2 images (C and D, respectively)**

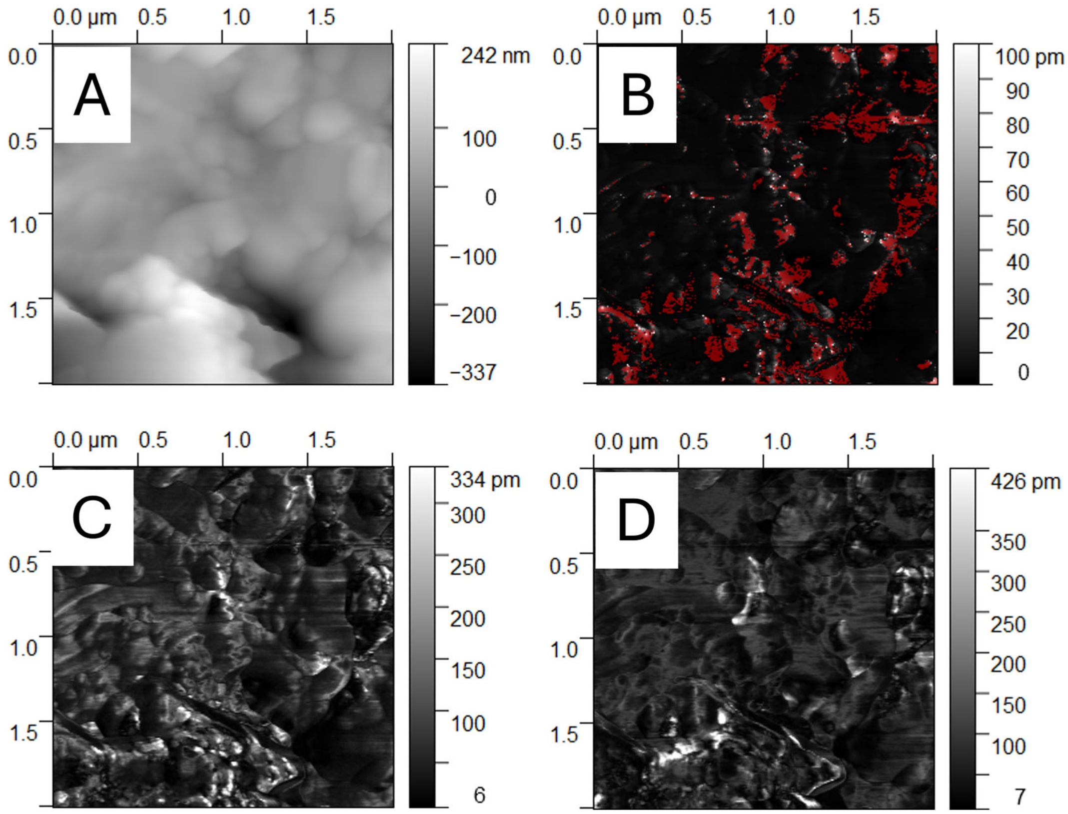

Fig. 4 Commercial height image (A) from DART-PFM using 1V-applied bias and the corresponding Ao image from the SHO model (B) using A1 and A2 images (C and D, respectively)

Figure 5 shows all five (bias voltage level) images of the height and corresponding Ao images for the ARL sample. When the bias voltage increases (moving down the series), the fraction of red pixels increases, which indicates worsening of fit by the SHO model. Figure 6 shows the same height and Ao images, with similar behavior, for the commercial sample. It is interesting to note that, for both samples, the height data also becomes “noisier” as the applied AC bias increases. In addition, qualitatively, it appears that many of the red pixels originate from boundaries in between crystals. This makes sense intuitively because the lower response is expected at a crystal boundary as opposed to the response at a crystal face.

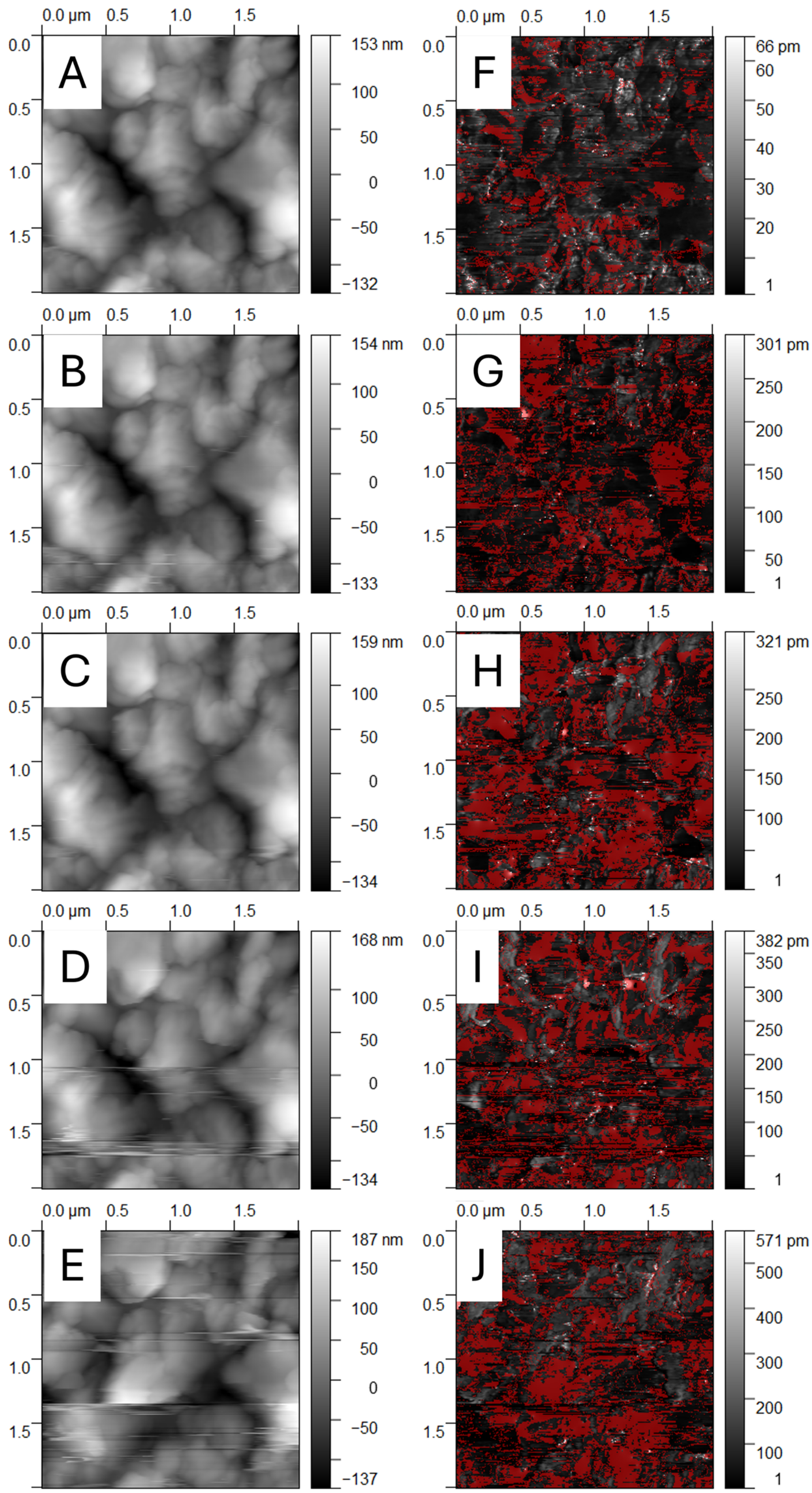

Fig. 5 ARL height images and the corresponding Ao from DART-PFM SHO for each applied bias (A–E and F–J are 1, 2, 3, 4, and 5V, respectively)

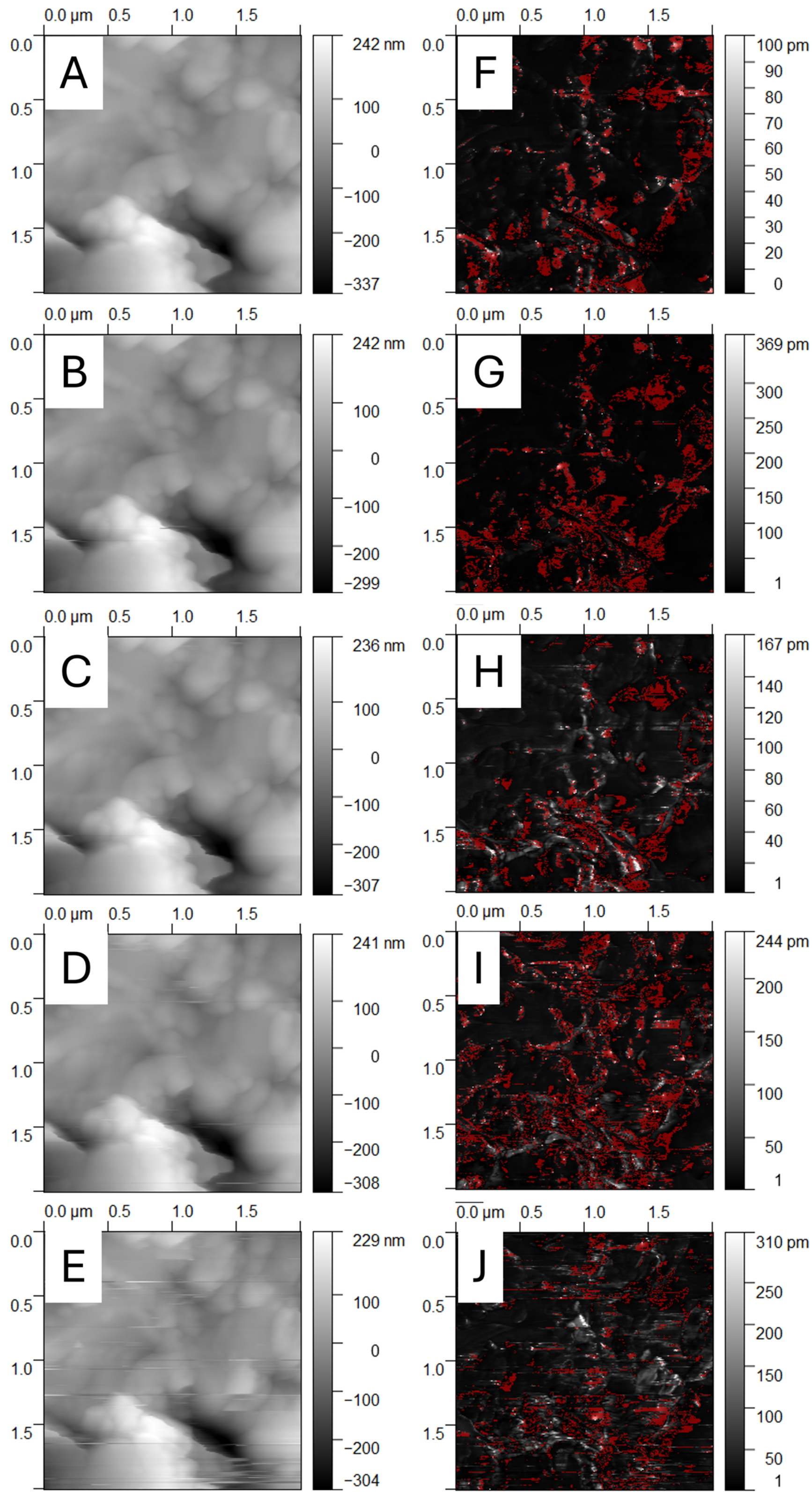

Fig. 6 **Commercial height images and the corresponding Ao from DART-PFM SHO for each applied bias (A–E and F–J are 1, 2, 3, 4, and 5V, respectively)**

Figure 7 shows the height images for both the ARL and commercial samples at the 1V-applied AC bias level for each tip. The imaging locations are selected at random. It is apparent that the ARL sample has a slightly more fine crystal size and therefore more edges in the scan area than the commercial sample. Each sample appeared to have consistent morphological features throughout their series: ARL samples had smaller features and commercial samples had larger features.

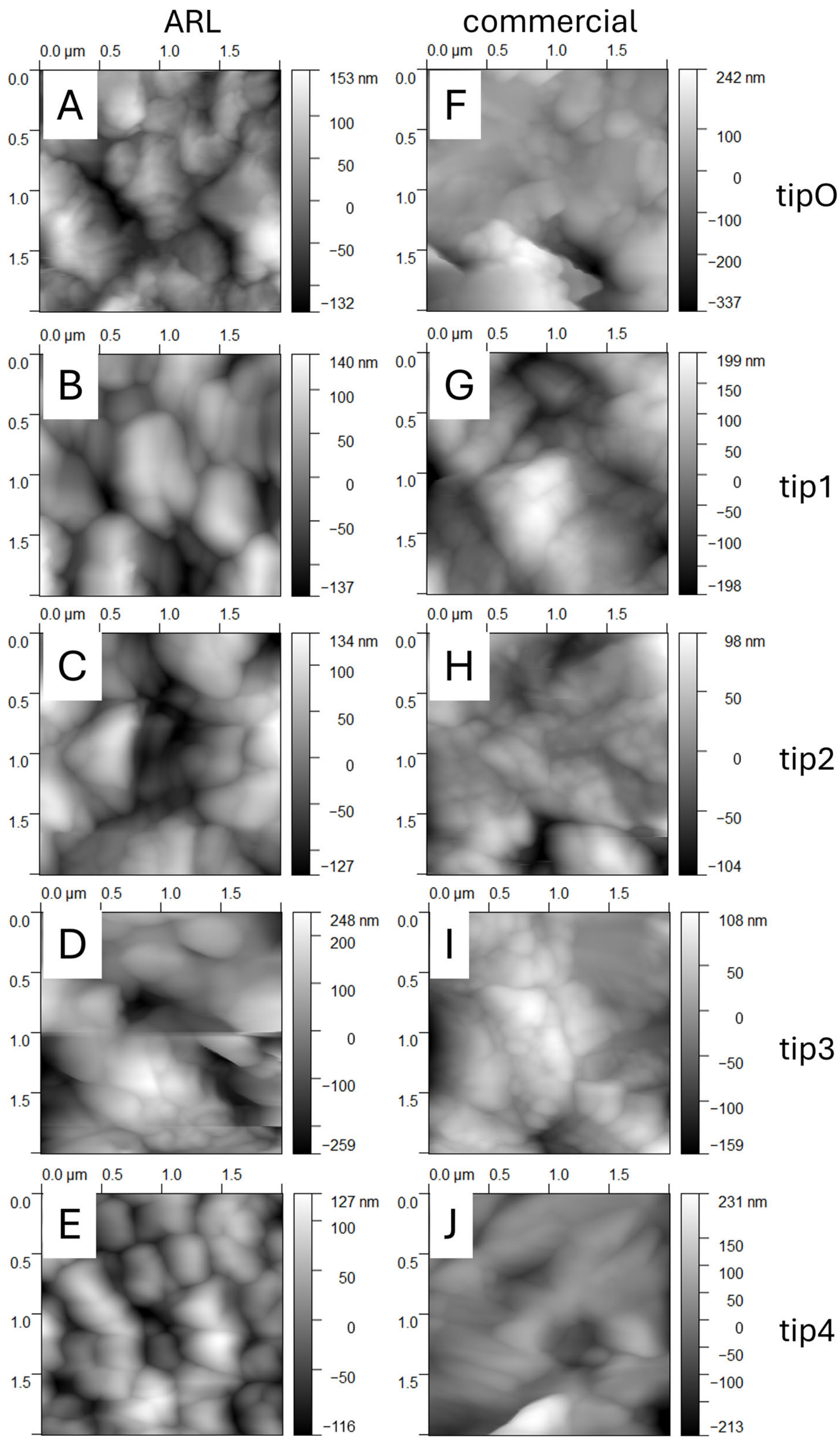

Fig. 7 Height at 1V for each tip and sample type from DART-PFM: A and F, tipO; B and G, tip1; C and H, tip2; D and I, tip3; E and J, tip4

3.3 Discussion

To assess the applicability of the DART-PFM technique, Ao images generated in the SHO model (from A1 and A2) were thresholded like the SF-PFM case (50th, 75th, 90th, 95th, and 99th percentile levels were measured). This is illustrated in the bar graphs in Fig. 8A and B for the ARL and commercial samples, respectively, using tipO. These data also show that as the bias voltage increases, so does the piezo response, in both samples. Note that there is appreciable and quantitative change in the Ao signals at these threshold percentages, where the Ao signal increases with bias voltage (for this particular probe, tipO). The effective d33 for the ARL and commercial samples at these bias voltages (Fig. 8C and D, respectively) appears to be relatively constant across the full bias range studied for both series. This is a positive result because it is the expected behavior. The d33 values should be a constant with respect to applied bias voltage.

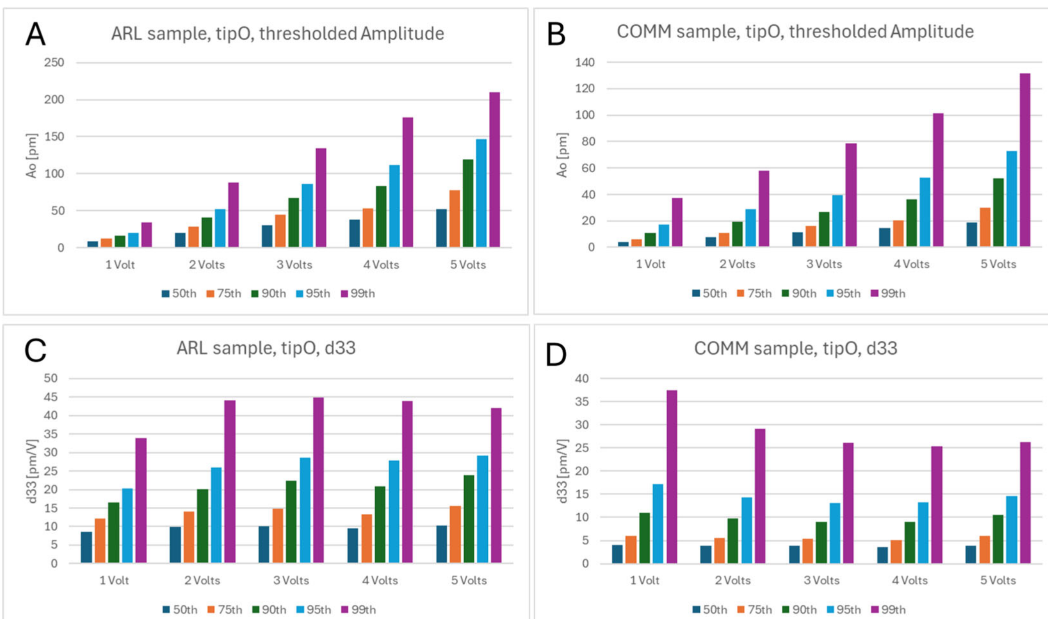

Fig. 8 (A and B) Amplitude (Ao) thresholds (50th, 75th, 90th, 95th, and 99th percentile) from DART-PFM at all applied bias values (ARL sample and commercial sample, tipO). (C and D) Corresponding d33 values, by taking ratio of Ao/applied bias voltage (ARL sample and commercial sample, tipO).

It is good to test samples with different probes to ensure the repeatability of results. Therefore, this testing was repeated (after tipO) using tip1, tip2, tip2, and tip4. In essence, this experiment was performed five times, to understand the repeatability of measurements. Rather than repeat the results from every tip, this analysis will include a summary of all results. Table 1 shows the error values of the d33 values under the assumption that d33 should be constant with repsect to applied bias voltage. Therefore, the standard deviation is taken as a percentage of the average of all d33 values across the voltage range 1–5V, for each tip.

Table 1 Error percentages: d33 standard deviation as a percentage of d33

	COMMtipO	ARLtipO	COMMtip1	ARLtip1	COMMtip2	ARLtip2	COMMtip3	ARLtip3	COMMtip4	ARLtip4
50th	4	7	31	22	52	13	44	34	19	12
75th	7	9	20	32	48	21	33	21	10	7
90th	9	13	12	39	48	27	24	15	11	7
95th	11	14	10	40	49	28	21	17	11	9
99th	17	11	10	40	44	23	14	24	16	9

The data from Table 1 is shown graphically in Fig. 9. The graphical representation shows that tipO and tip4 experiments resulted in the most consistent values of d33 (lowest relative standard deviations). Note also that the 75th percentile data produced the lowest error percentages by this measure. In all four cases of tipO (Fig. 9, ARL and COMM) and tip4 (Fig. 9, ARL and COMM), the 75th percentile always has a less than 10% error value. Therefore, the 75th percentile was selected as the benchmark threshold value in this study.

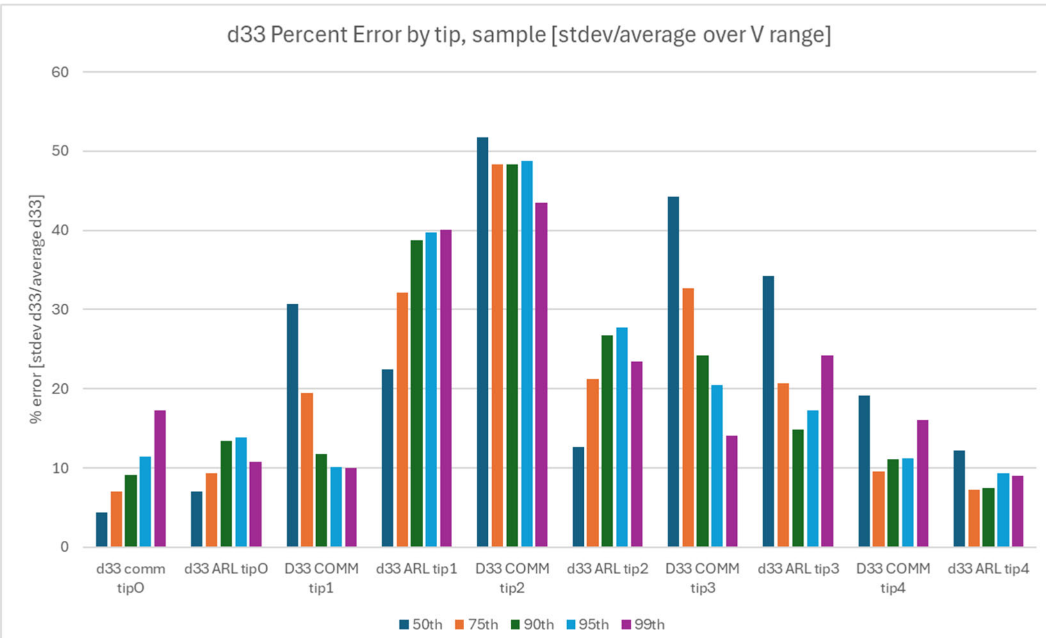

Fig. 9 Percentage error in d33 values from all tips, samples. Percentage error is defined as (standard deviation of d33/average value of d33) × 100.

Figure 10 shows the results from all four tips where the d33 value is an average of d33 from all five AC bias voltages, and the error bars represent the standard deviation of those values. As noted, tipO and tip4 have the smallest standard deviations relative to their averages. It is interesting to note that the commercial sample has almost the same effective d33 when measured by tipO and tip4;

however, the ARL sample shows a large difference when measured by these probes. According to TipO, the d33 values for the ARL sample is larger than d33 for the commercial sample, whereas according to tip4, the commercial d33 is larger.

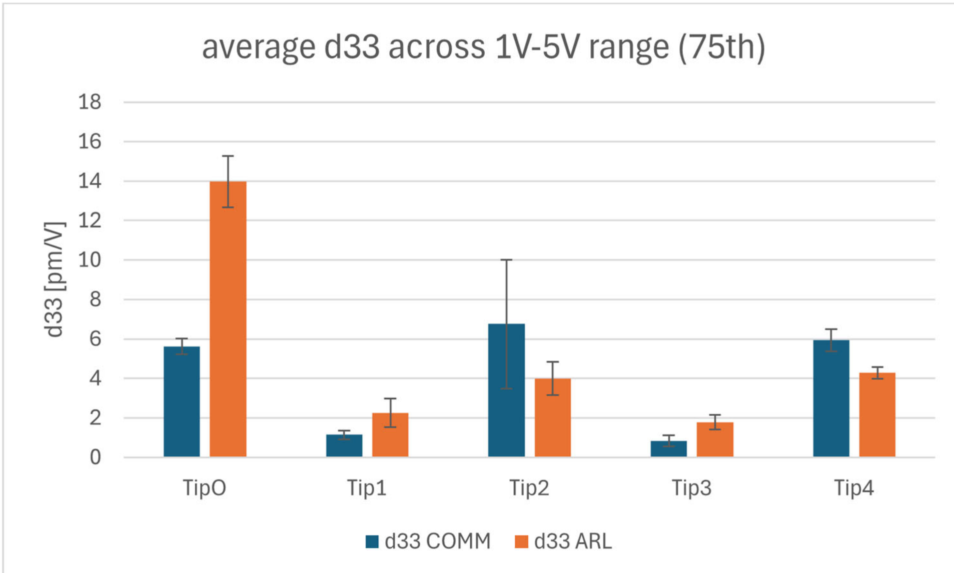

Fig. 10 Average d33 across the full voltage range (1–5V) for both samples (ARL and commercial)

Finally, part of the goal of this work is to compare two similar materials which have different processing history. Therefore, a ratio of d33 values (ARL/commercial) at each voltage is plotted in Fig. 11 for each tip used (A–E, tipO, tip1, tip2, tip3, and tip4, respectively). For tipO, tip1, and tip3, the plots show that the ratio (ARL/commercial) is greater than 1, indicating that the ARL sample has a higher d33 value. On the other hand, tip2 and tip4 indicate the reverse: the commercial sample has a larger d33 value. The tipO and tip4 were the lowest relative error datasets, but when comparing the d33 values they give disparate results. Therefore, more study is needed to reduce the sources of error in the methodology so that materials can be compared.

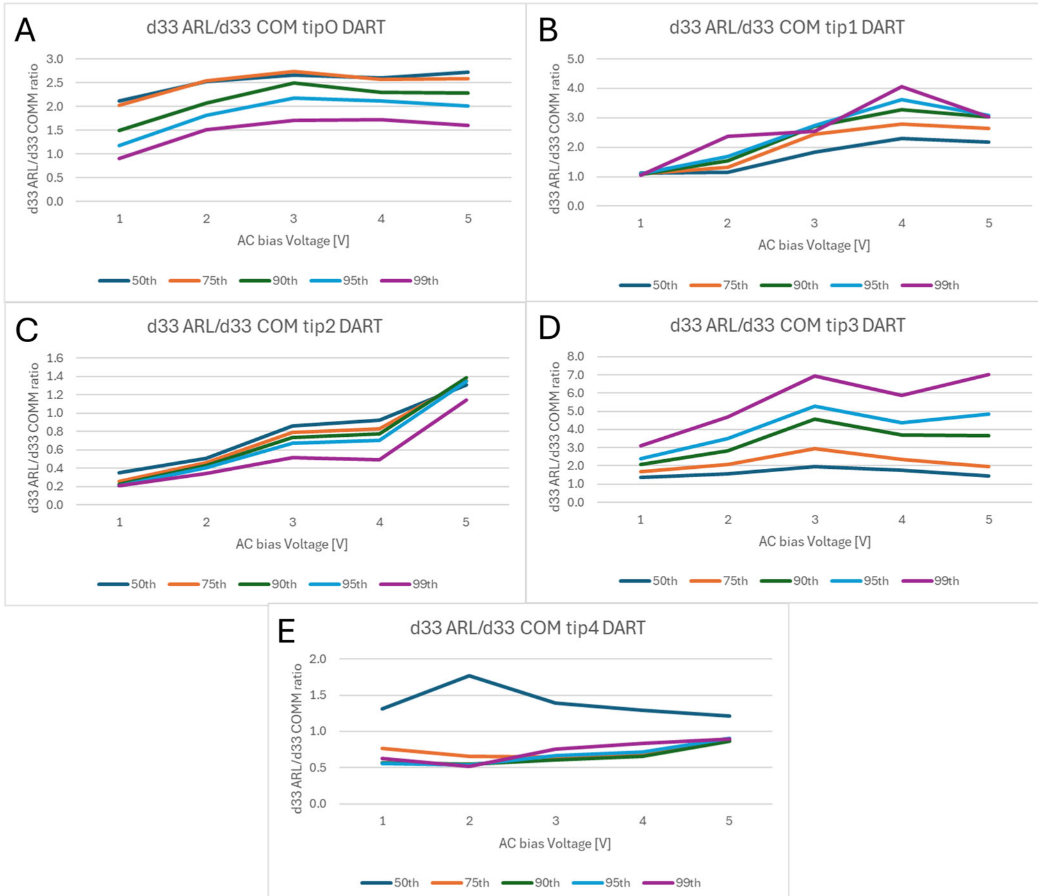

Fig. 11 Ratio of (d33 ARL/d33 commercial) at each AC bias voltage for all five of the tips

4. Conclusion

This study included the creation of two methodologies for local piezoresponse measurements of piezo-responsive materials using an AFM, including single-frequency PFM and DART-PFM. The methodologies were created to determine whether they were capable of 1) detecting and quantifying a piezoresponse and 2) comparing the quantitative piezoresponse of different materials. Five different probes and two different materials were used in this study.

This study also showed that SF-PFM is not an appropriate measurement methodology for studying the materials selected. The signal-to-noise ratio and sources of error were apparently poor enough that it was not possible to quantifiably detect a piezoresponse from these materials. On the other hand, DART-PFM was able to qualitatively and quantitatively measure the piezoresponse of the materials compared. The benefit of this latter methodology was that the response signal was quantitatively larger than the noise. One drawback of DART-PFM was that after fitting to the SHO model, some parts of the data were lost due to poor fitting.

Another drawback was that through the five probes we used, three of them indicated that the ARL sample had larger d33, whereas the other two indicated that the commercial sample had larger d33. Therefore, further careful study is suggested to develop the DART-PFM methodology.

For future studies, we suggest careful sample preparation, including polishing and pressing of samples to reduce topography. In addition, we suggest the use of various probes to understand the effect of probe selection. Finally, we suggest 1) a scan of multiple scan areas and 2) larger scan areas to determine the distribution of d33 behavior within each sample.

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List of Symbols, Abbreviations, and Acronyms

AC	alternating current
AFM	atomic force microscopy
AMP	amplitude
ARL	Army Research Laboratory
COMM	commercial
DART	dual-AC resonance tracking
DC	direct current
DEVCOM	US Army Combat Capabilities Development Command
KNN	potassium sodium niobate (K, Na, or NbO_3)
PFM	piezoresponse force microscopy
pm/V	inverse piezoelectric coefficient
PZT	lead zirconate titanate
SF	single frequency
SHO	simple harmonic oscillator
tipO	original tip
V	volt

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