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Bending characteristics of ferroelectric poly(vinylidene fluoride trifluoroethylene) capacitors fabricated on flexible polyethylene naphthalate substrate

Sung-Min Yoon [a,*], Soon-Won Jung [b], Shinhyuk Yang [b], Sang-Hee Ko Park [b], Byoung-Gon Yu [b], Hiroshi Ishiwara [c,d]

[a] Department of Advanced Materials Engineering for Information and Electronics, Kyung Hee University, 1 Seocheon-dong, Giheung-gu, Yongin-si, Gyeonggi-do 446-701, Republic of Korea
[b] Convergence Components & Material Research Laboratory, Electronics and Telecommunications Research Institute (ETRI), 138 Gajeong-no, Yuseong-gu, Daejeon 305-700, Republic of Korea
[c] Tokyo Institute of Technology, 4259, Nagatsuta, Midori-ku, Yokohama 226-8502, Japan
[d] Department of Physics, Konkuk University, 1 Hwayang-dong, Gwangin-gu, Seoul 143-701, Republic of Korea

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A B S T R A C T

Ferroelectric capacitors using poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] were fabricated on the plastic polyethylene naphthalate (PEN) substrate for the various applications of flexible-type nonvolatile memories. It was successfully confirmed that the Au/P(VDF-TrFE)/Au capacitors showed sound ferroelectric characteristics even when they were fabricated using a lithography-compatible patterning process at low temperature below 150 °C in the PEN. The behaviors of ferroelectric polarization and saturation as a function of the applied electric field were not so sensitive to the changes in bending curvature radius. However, because small variations in switching properties for the polarization reversal were also observed especially for higher frequency and lower voltage regions, suitable operation schemes should be designed for the flexible memory devices with lower voltage and higher speed operations even at bending situations.

1. Introduction

In realizing highly functional electronic systems integrated on bendable or rollable plastic substrates, the embeddable nonvolatile memory device is one of the most demanding elements. Actually, in recent days, various types of interesting approaches to new paradigm of consumer electronics have been vigorously researched and developed, such as radio frequency indentification tags [1–3], flexible sensor arrays [4–6], flexible and stretchable displays [7–9], flexible electronic circuits [10–12], and sheet-type communication system [13]. Furthermore, the employment of suitable nonvolatile memory device can also effectively reduce the power consumption of display panel [14,15]. Therefore, if we can provide the memory device having features of mechanical flexibility, lower power operation, and higher device reliability with a simpler process at lower temperature, it would have a great impact on the related industries. So far, various methodologies with different operating origins have been tried to fabricate memory devices on the flexible plastic substrates. They were (1) resistance change types using redox reaction in organic layers [16,17] or filament formation between the electrodes [18], (2) charge injection types having such structures as organic bilayer devices [19] or nanoparticle embedded organic layers [20,21], (3) floating-gate type transistors using organic semiconducting active channels [22,23], and (4) ferroelectric-based thin-film transistors (TFTs) [24,25]. Among them, the ferroelectric field-effect TFT employing a typical ferroelectric copolymer of poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] is a very promising candidate because they can be prepared with a definitely designable operation principle and a very simple process. However, for the flexible memory applications, the variations in intrinsic ferroelectric natures of the P(VDF-TrFE) thin film should be systematically investigated when the devices were fabricated and treated on the plastic substrates. Especially, it is very important to confirm what happens to the electrical characteristics, such as the ferroelectric remnant polarization (P_r) and coercive field (E_c), of the (PVDF-TrFE) under mechanical bending situations of the substrate [26,27]. It was very interesting that the combination of stretching to plastic deformation and thermal annealing dramatically could reduce the surface roughness and leakage current of the P(VDF-TrFE) on the plastic [27]. In this work, the P(VDF-TrFE) ferroelectric capacitors were

* Corresponding author. Tel.: +82 31 201 3617; fax: +82 31 204 8114.
E-mail address: sungmin@khu.ac.kr (S.-M. Yoon).

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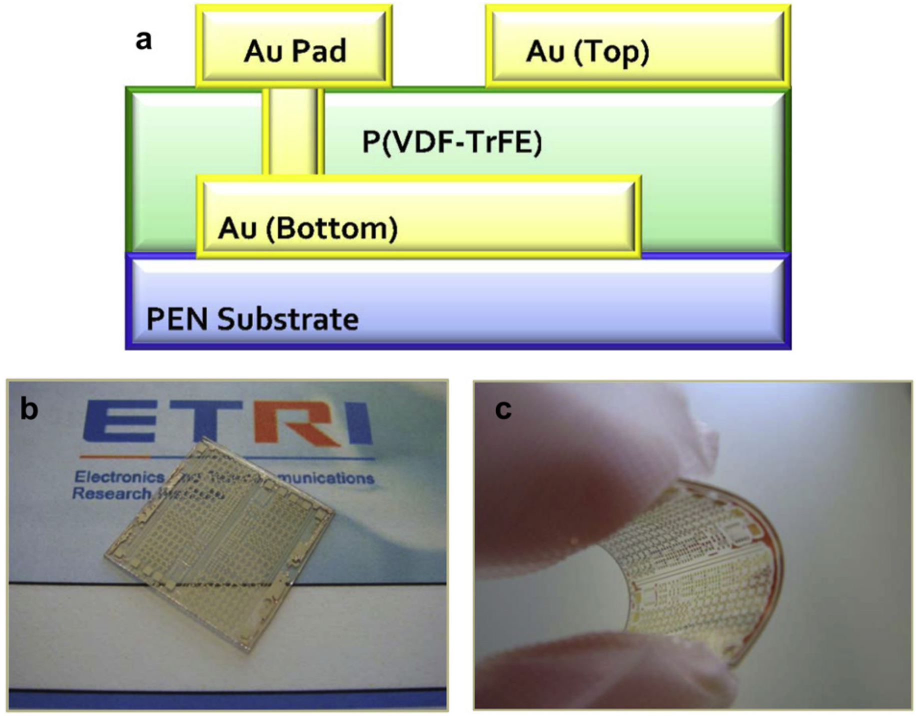

Fig. 1. (a) Schematic cross-sectional diagram of the fabricated P(VDF-TrFE) capacitors and (b) photograph of the PEN substrate on which Au/P(VDF-TrFE)/Au capacitors were fabricated. (c) A typical photo image of the PEN substrate under a bending situation.

fabricated on the plastic substrate by employing the fully lithography-compatible patterning process and electrically characterized when the devices were mechanically bent with given radius curvatures in a more systematic way. These investigations provide us useful insights related to the appropriate operation schemes for realizing the ferroelectric-based embeddable flexible memory onto the plastic substrate.

2. Experimental details

Ferroelectric P(VDF-TrFE) capacitors were fabricated on the flexible poly(ethylene naphthalate) (PEN) substrate (Teonex, Teijin DuPont). PEN substrate has such good characteristics as low coefficient of thermal expansion, low water absorption, strong chemical resistance, and low cost for the flexible device fabrication, although its optical transmittance at the visible range is reported to be relatively low (approximately 80%). The thickness and size of the PEN substrate employed in this work was 200 μm and $2 \times 2\ cm^2$, respectively. During the process, two important considerations were mainly verified. The first one was to confirm the feasibility of applying the conventional lithography-compatible process to the PEN substrate. The align margin between the process layers is very sensitively affected by the expansion and shrinkage of plastic substrate (PEN in this work) during the thermal process. The second one was to suppress the thermal budget of the overall process to be lower than 150 °C, even though the employed PEN

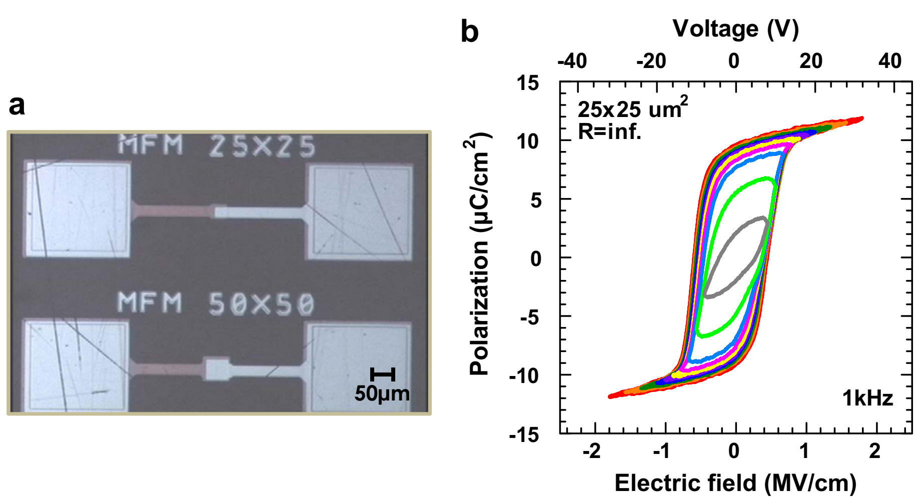

Fig. 2. (a) Microscopic top view of the Au/P(VDF-TrFE)/Au capacitors fabricated on PEN with fully lithography-compatible patterning process. (b) A typical *P*–*E* characteristics of the fabricated capacitor with the size of $25 \times 25\ \mu m^2$ at the frequency of 1 kHz.

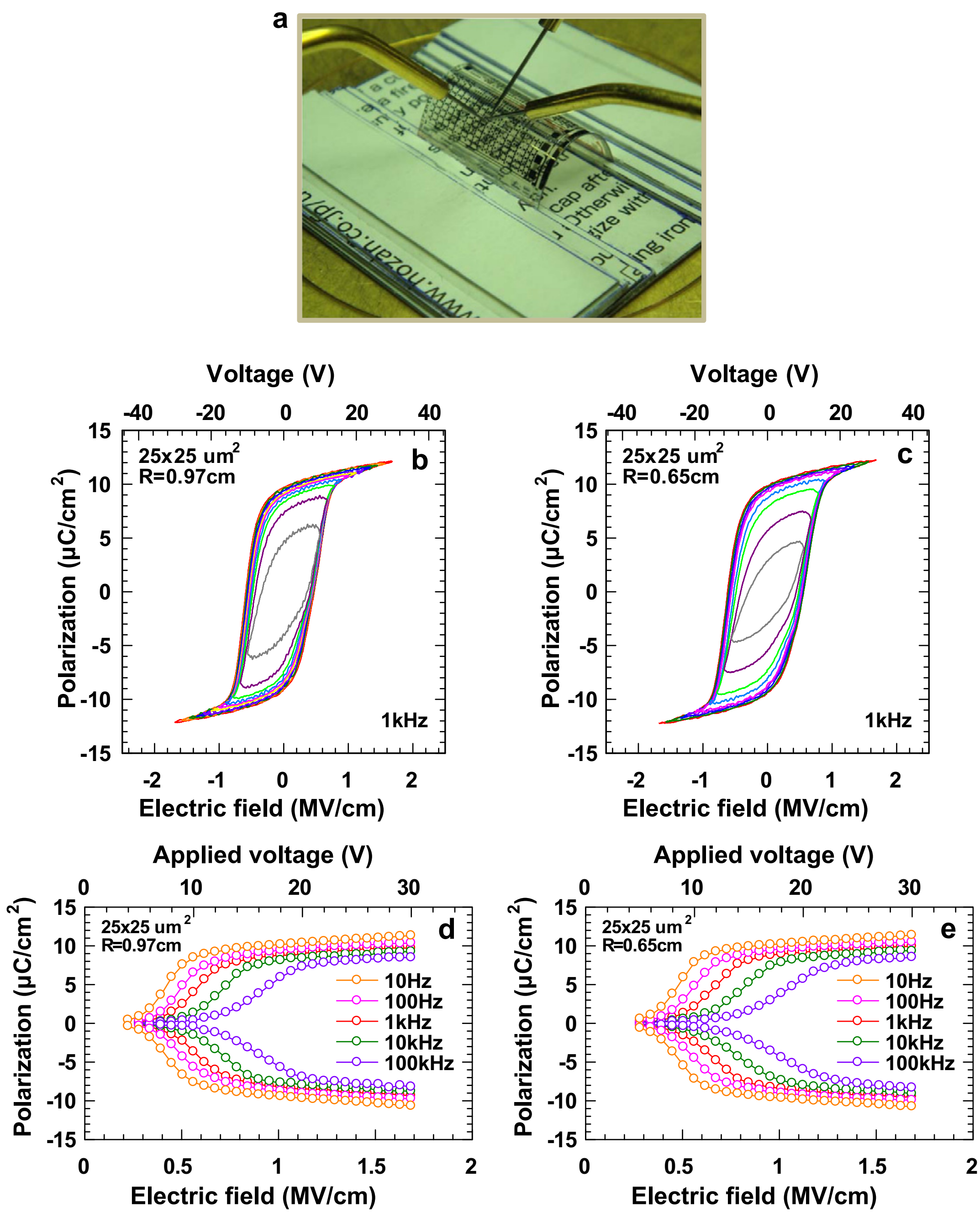

Fig. 3. (a) Photo-image of electrical evaluations when the substrate was bent ($R = 0.65$ cm). *P–E* characteristics of the Au/P(VDF-TrFE)/Au capacitor when the substrate was bent with different *R*'s of (b) 0.97 and (c) 0.65 cm. The measurement frequency was set to be 1 kHz. Polarization saturation behaviors with the increase of applied electric field at various signal frequencies from 10 Hz to 10 kHz for the bending situations with *R*'s of (d) 0.97 and (e) 0.65 cm.

was guaranteed in mechanically using at 160 °C. Fabrication procedures were performed as follows. Firstly, bottom electrodes of Au were deposited by thermal evaporation and patterned via lift-off method. P(VDF-TrFE) thin film was formed by conventional spin-coating method using a 3 wt% diluted solution of powder-type P(VDF-TrFE) (70/30 mol%, Solvay Solexis) in methyl-ethyl-ketone (MEK). Solutions were spun-on the substrate at a spin rate of 2000 rpm for 10 s and dried at 70 °C for 10 min in a hot plate. The coated film was treated at 140 °C for 1 h for its crystallization. The resultant film thickness was approximately 180 nm, which was measured by surface profiler (α-step, KLA Tencor). The via-hole for contact to bottom electrode was opened by etching the given area of P(VDF-TrFE) film by using O_2 plasma with a reactive ion etching system (Samco RIE-10NL). Then, the Au top electrode and bottom electrode pad were formed by the lift-off process. Fig. 1(a) and (b) show a cross-sectional schematic diagram and a photo image for the Au/P(VDF-TrFE)/Au capacitors fabricated on the PEN substrate. The processed substrate can be also bendable as shown in Fig. 1(c). The fabricated ferroelectric P(VDF-TrFE) capacitors were characterized by a ferroelectric capacitor evaluation system (FCE, Toyo Technica). All measurements were carried at room temperature in a dark box.

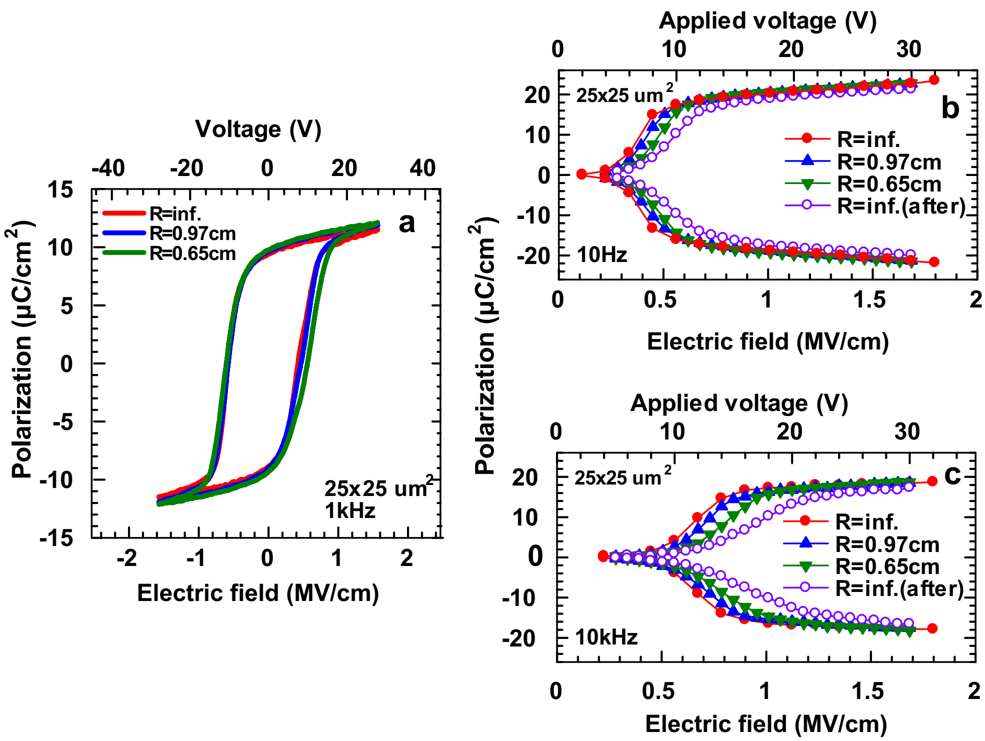

Fig. 4. Comparisons of the (a) ferroelectric *P*–*E* characteristics at the applied voltage of 30 V and the polarization saturation behaviors with increase in the applied electric field at the signal frequencies of (b) 10 Hz and (c) 10 kHz when the *R* was varied to ∞, 0.97, and 0.65 cm. The polarization saturation characteristics were also evaluated when the substrate was restored to the original state of infinite *R*. The capacitor size was 25 × 25 μm^2.

3. Results and discussions

Fig. 2(a) shows a top-view of optical microscope image for the ferroelectric P(VDF-TrFE) capacitors fabricated on the PEN. The capacitors with the sizes of 25 × 25 and 50 × 50 μm^2 were accurately defined between the top and bottom electrode pads. The polarization-electric field (*P*–*E*) characteristics of the Au/P(VDF-TrFE)/Au capacitor with the size of 25 × 25 μm^2 were evaluated as shown in Fig. 2(b) when the *E* was varied from 0.45 to 1.80 MV/cm. The remnant polarization (P_r) and coercive field (E_c) were typically measured to be approximately 9.1 μC/cm^2 and 522 kV/cm, respectively, at the frequency of 1 kHz. Obtained characteristics were found to be almost comparable to those for the P(VDF-TrFE) capacitors fabricated on the glass or Si substrates. It was confirmed that the ferroelectric P(VDF-TrFE) capacitors showed sufficiently good properties even on the PEN substrate, and that the lithography-compatible patterning processes could be carried out without any critical problems on the flexible PEN.

Next, the variations in electrical properties of the fabricated capacitors were evaluated when the substrate was bent with a given curvature radius (*R*). A series of measurements was performed by setting the proving system, as described in Fig. 3(a). Fig. 3(b) and (c) show the *P*–*E* characteristics of the same capacitor evaluated in Fig. 2 when the substrate was bent with two different *R*'s of 0.97 and 0.65 cm, respectively. The P_r was varied from approximately 9.4–9.6 μC/cm^2 with the decrease in *R*'s from 0.97 to 0.65 cm. Although the P_r at *R* of 0.65 cm was observed to increase by 5% compared with the case when *R* was infinite (∞), it did not experience a significantly marked variation. This situation can be well confirmed in Fig. 4(a), in which ferroelectric hysteresis curves obtained at the same field for the situations with different *R*'s were compared at the same plane. The small increase in P_r probably originated from the increase in leakage current component for the evaluated capacitor owing to the repeated measurements at a high electric field. On the other hand, the E_c was measured to be approximately 528 and 588 kV/cm at *R*'s of 0.97 and 0.65 cm, respectively. It was found that there was approximately 13% increase in E_c, especially when the substrate was bent with *R* of 0.65 cm, as compared in Fig. 4(a). It is more reasonable to conclude that the origins of increase in E_c was not the mechanical strain induced by the substrate bending but some degradations in electrical behaviors during the repetitive measurements, that is a kind of fatigue.

The polarization saturation behaviors with the increase in *E* applied across the P(VDF-TrFE) film were also estimated with the variations of signal frequency from 10 Hz to 100 kHz. The fact that the *E* required to obtain the full saturation in *P* decreased with the decrease in the frequency is typically observed for the ferroelectric capacitors using P(VDF-TrFE) copolymers, which is closely related to the fact that the switching time of ferroelectric polarization is sensitively affected by the duration of applied voltage signals as well as the voltage amplitude [28–30]. These general characteristics were also confirmed for the cases when the devices were intentionally bent with given *R*'s of 0.97 and 0.65 cm, as shown in Fig. 3(d) and (e), respectively.

The detailed effect of bending radius on the polarization saturation behaviors can be shown in Fig. 4(b) and (c), in which the evolution of increase in P_r at two signal frequencies of 10 Hz and 10 kHz was compared, respectively, when the *R* was varied to ∞, 0.97 and 0.65 cm. Here, in order to quantitatively compare the characteristics of each situation, it is very useful to introduce a parameter, $E_{hp.}$ The E_{hp} was defined as the electric field required for approaching to the half point of full saturation state of ferroelectric polarization (0.5 P_r) under the bending status of the P(VDF-TrFE) capacitors at a given signal frequency. For the case when the properties were evaluated at the frequency of 10 Hz [Fig. 4(b)], the

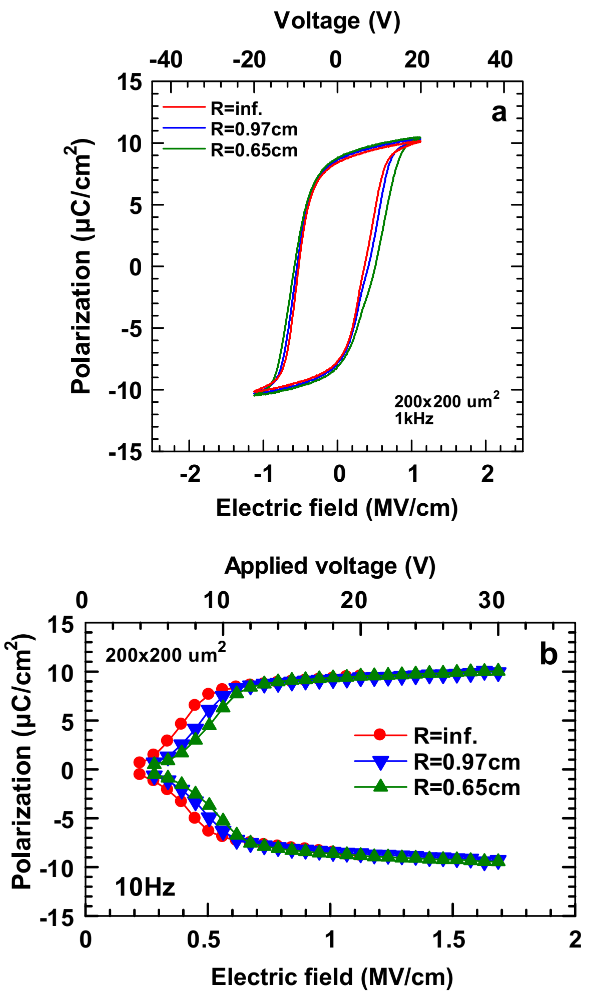

Fig. 5. Comparisons of the (a) ferroelectric *P*–*E* characteristics at the applied voltage of 20 V and the (b) polarization saturation behaviors at the signal frequencies of 10 Hz for the Au/P(VDF-TrFE) capacitor with the size of 200×200 μm^2 when the *R* was varied to ∞, 0.97, and 0.65 cm.

values of E_{hp} for the situations with *R* of ∞, 0.97, and 0.65 cm were estimated to be approximately 0.38, 0.41, and 0.44 MV/cm, respectively. On the contrary, the E_{hp}'s at the frequency of 10 kHz [Fig. 4(b)] were approximately 0.67, 0.72, and 0.81 MV/cm for the cases with *R* of ∞, 0.97, and 0.65 cm, respectively. It can be supposed from these results that the initial switching event of polarization reversal might be impeded when the devices were under the bending situations, and that the extent of impediment might be larger for the cases of larger *R* and higher signal frequency. However, when the substrate was restored to the original status of infinite *R*, the parameters of E_{hp} were observed to show larger values than those for the case with *R* of 0.65 cm, as shown in Fig. 4(b) and (c). Even though some parts of E_{hp} degradation caused by the mechanical strain at bending situation cannot be completely ruled out yet, the obtained results strongly suggest that the larger impediment in polarization reversal observed for the larger *R* was also dominantly affected by the ferroelectric fatigue. Because these kinds of evaluation are sometimes very tricky, more detailed investigations including iterative examination and data reproducibility will be carried out as future works. It is also interesting to note that there were not so large variations in *E* required for the full saturation of *P*. These behaviors are probably related to the intrinsic changes in initial nuclei formation event for the polarization reversal and practically influence the device operations especially for lower voltage region.

It was found from previously discussed insights that the mechanical strain induced to the P(VDF-TrFE) capacitors under the bending situation did not make any decisive impact on the ferroelectric behaviors of the fabricated devices. This conclusion is in a good agreement with the previous demonstrations [26,27]. The investigations of capacitor size dependency on the bending characteristics can reflect this consideration. The mechanical strain will be differently induced for the capacitors with different size even for the same *R*. The *P*–*E* characteristics of the P(VDF-TrFE) capacitor with the size of 200×200 μm^2 were evaluated when the *R* was varied to ∞, 0.97, and 0.65 cm, as shown in Fig. 5(a). There was no marked difference in behaviors except for the small increase of E_c with the decrease of *R*, which was similarly observed for the case of 25×25-μm^2-sized capacitor. The E_{hp}'s measured at 10 Hz for the *R*'s of ∞, 0.97, and 0.65 cm were 0.39, 0.44, and 0.49 MV/cm, respectively, as shown in Fig. 5(b). It suggests the polarization saturation was also found to behave in a very similar way to those shown in Fig. 4(b) even for the larger capacitor size.

4. Conclusions

In order to confirm the feasibility of P(VDF-TrFE)-based flexible memory devices and investigate their bending characteristics, the ferroelectric capacitors with the structure of Au/P(VDF-TrFE)/Au were fabricated on the plastic PEN substrate. The sound characteristics of ferroelectric natures for the fabricated capacitors were well confirmed, which was of significance in that they were obtained with the fully lithography-compatible patterning process at low temperature below 150 °C. The ferroelectric polarization behaviors such as *P*–*E* characteristics and saturation trends with the increase in *E* were found to be not so sensitively changed with the variation in the curvature radius under the substrate bending conditions. However, small changes in switching events for the polarization reversal at higher frequency and lower voltage regions could not be completely ruled out especially when the larger *R* was applied. These obtained results provide useful insights to design the low cost flexible memory with excellent performances such as lower voltage and higher speed operations even when the devices are mechanically bent with given *R*'s for various applications.

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