Transient Response of Negative Capacitance in P(VDF$_{0.75}$-TrFE$_{0.25}$) Organic Ferroelectric Capacitor

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ABSTRACT The transient response of negative capacitance (NC) in an organic ferroelectric capacitor is experimentally investigated. To observe the transient response of the NC, a simple series network, consisting of an external series resistor and an organic ferroelectric capacitor, is built. The Landau coefficients of the organic ferroelectric capacitor were extracted from the measured polarization versus applied electric field data. A circuit level simulation was provided with the extracted parameters based on the Landau–Khalatnikov equation. To explore the impact of the RC time constant on the NC time duration in the RC series circuit, the external series resistor is altered as a tuning parameter. Also, the effect of various temperatures of the ferroelectric capacitor on the NC time duration is experimented. This paper demonstrates that either the external resistor or the ambient temperature can change the NC time duration in an organic ferroelectric capacitor.

INDEX TERMS Negative capacitance, ferroelectrics, transient response, negative capacitance field effect transistor, NCFET, organic ferroelectric capacitor.

I. INTRODUCTION

Negative capacitance in a ferroelectric capacitor (i.e., $C_{FE} = dQ/dV < 0$, where Q is the charge and V is the voltage across a capacitor) was theoretically suggested as a promising solution to surmount the Boltzmann limit in metal-oxide semiconductor field-effect transistors (MOSFETs) (i.e., the subthreshold slope (SS) is, at best, 60 mV/decade at 300 K) [1]. Afterwards, a sub-60-mV/decade steep-switching MOSFET with internal voltage amplification due to negative capacitance (i.e., the surface potential of the MOSFET was higher than the applied gate voltage) was experimentally demonstrated [2]–[12]. In this work, to explicitly verify the existence of negative capacitance in an organic ferroelectric capacitor, the negative capacitance in the organic ferroelectric capacitor with amorphous copolymer of P(VDF$_{0.75}$-TrFE$_{0.25}$) was directly measured using a simple R-C$_{FE}$ series circuit at various temperatures and/or with various external resistors.

Because of the benefits of organic ferroelectric polymers [e.g., polyvinylidene fluoride (PVDF)], such as eco-friendliness (lead-free) and low cost of fabrication, they are used in many applications, including negative-capacitance field-effect transistors (NCFETs) [2]–[7]. However, a direct observation of negative capacitance in organic ferroelectric capacitor has not yet been reported, whereas the negative capacitance in inorganic ferroelectric capacitors using single crystalline thin film of Pb(Zr$_{0.2}$Ti$_{0.8}$)O$_3$ (PZT) has been reported [13], [14].

To observe the negative capacitance in an organic ferroelectric capacitor, an external resistor is connected in series to the organic ferroelectric capacitor, similar to a conventional RC series circuit. Then, we investigate whether the RC time constant in the R-C$_{FE}$ circuit controls the dynamics of charging and discharging the organic ferroelectric capacitor. To observe the effect of various RC$_{FE}$ time constants on the transient response of the R-C$_{FE}$ circuit, either various external resistors or different temperatures for the organic ferroelectric capacitor are used in the RC$_{FE}$ circuit.
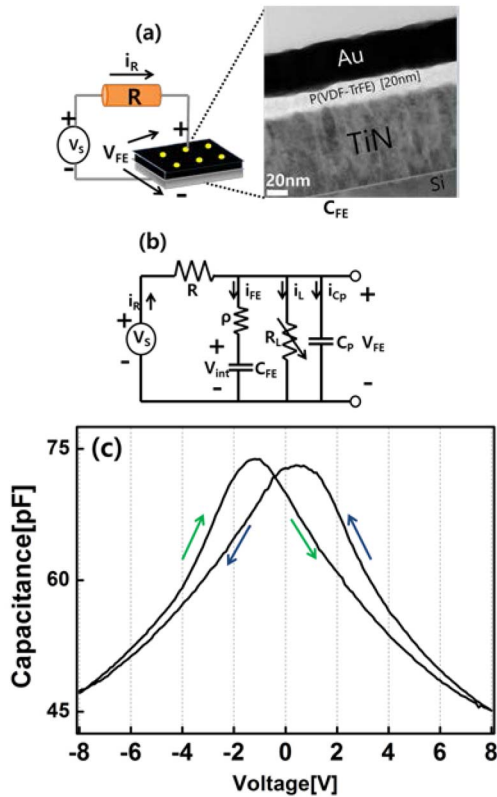
FIGURE 1. (a) Circuit schematic of R-C$_{FE}$, in which V$_{S}$, R, i$_{R}$, V$_{FE}$, and C$_{FE}$ indicate the source voltage, the series resistor, the current through R, the voltage across C$_{FE}$, and the capacitance of the ferroelectric capacitor, respectively. (b) Equivalent electrical circuit for Landau-Khaltnikov simulation model: ρ is the internal resistance, i$_{FE}$ is the current through C$_{FE}$, V$_{int}$ is the internal voltage, R$_{L}$ is the leakage resistance, i$_{L}$ is the current through R$_{L}$, C$_{P}$ is the parasitic capacitance, and i$_{Cp}$ is the current through C$_{P}$. (c) Measured capacitance–voltage of the isolated organic ferroelectric capacitor.

II. FABRICATION AND MEASUREMENT

To observe the transient response of negative capacitance, a basic RC series network, consisting of an external resistor and an organic ferroelectric capacitor, was set up [see Fig. 1(a)]. To fabricate the organic ferroelectric capacitor, a copolymer of polyvinylidene fluoride (PVDF) and trifluoroethylene (TrFE) was used as the solute in a 75/25 ratio, which represents outstanding polarization characteristics [15]. To make a 1 wt% solution of P(VDF$_{0.75}$−TrFE$_{0.25}$), methyl ethyl ketone (MEK) was used as the solvent. The solution was heated on a hot plate (60 °C) to completely dissolve the P(VDF$_{0.75}$−TrFE$_{0.25}$) powder. Then, the solution was spin coated on top of the 80-nm TiN layer for the bottom electrode, which was deposited on a bulk silicon substrate by DC magnetron sputtering, at 1500 rpm for 30 seconds to create the approximately 20-nm-thick organic ferroelectric insulation layer. The capacitor was annealed for 1 hour at 140 °C after spin coating. Since the high β phase crystallinity of P(VDF-TrFE) can be formed at around the Curie temperature, the annealing temperature was set at 140 °C [16], [17]. Finally, 42-nm-thick gold was
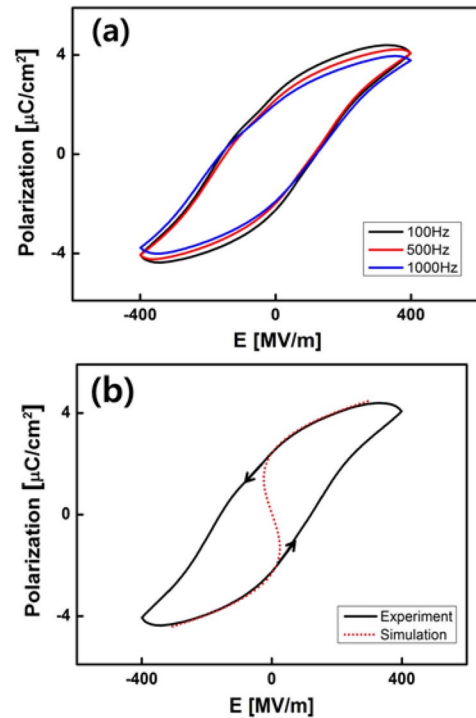

FIGURE 2. (a) Measured P-E curve at 100Hz, 500Hz, 1000Hz frequencies (b) Simulated P-E curve of the organic ferroelectric P(VDF$_{0.75}$-TrFE$_{0.25}$) capacitor.

patterned as a circle with a diameter of 0.2 mm for the top electrode, using thermal evaporation.

Figure 1(c) shows the measured capacitance value of the isolated ferroelectric capacitor at 1MHz, which ranges from 45 pF to 73 pF, using the Keithley 4200-SCS measurement system at room temperature. Gold wire was used to contact the ferroelectric capacitor. The coercive voltages from the measured capacitance–voltage are −0.9 V and 1.2 V. The difference between coercive voltages comes from the different work functions of Au and TiN electrodes [18]. Figure 2 shows the polarization (P) versus applied electric field (E) measured by the TF Analyzer 1000 at various frequencies [i.e., 100Hz, 500Hz, and 1000Hz] with the triangular wave [herein, the peak-to-peak voltage (V$_{PP}$) = 16 V]. The number of data points for each frequency is 400. Since the effects of defects in the isolated ferroelectric capacitor can be avoided at high frequency, coercive voltages were determined from the C-V data in Fig. 1(c). The parasitic capacitance (C$_{P}$) contributed by the oscilloscope and the Keithley 4200-SCS was extracted to be approximately 200pF.

III. RESULTS AND DISCUSSION

To quantitatively understand the physics of the negative capacitance in a ferroelectric material, the Gibb's free energy (U) for the ferroelectric capacitor/system is described in Eq. (1) as follows:

$$U = \alpha P^2 + \beta P^4 + \gamma P^6 - EP \qquad (1)$$

where U is the Gibb's free energy, P is the polarization, E is the externally applied electric field, and α, β and γ are the Landau coefficients for a ferroelectric material. Using the Landau-Khalatnikov (LK) equation [see Eq. (2)], Eq. (1) can be modified to Eq. (3).

$$\frac{dU}{dP} = -\rho \frac{dP}{dt} \tag{2}$$

$$E = 2\alpha P + 4\beta P^3 + 6\gamma P^5 + \rho \frac{dP}{dt} \tag{3}$$

Here, ρ is the dynamic parameter for time-dependent LK equation. On the other hand, α, β, and γ are the static parameters. In order to extract these static parameters of the 20nm-thick P(VDF$_{0.75}$-TrFE$_{0.25}$) capacitor, the polarization (P) versus applied electric field (E) was measured. Figure 2(b) shows the measured P-E curve and simulated P-E curve with the extracted parameters. Assuming the steady-state [i.e., $\frac{dP}{dt} = 0$ in Eq. (3)], Eq. (3) was used to extract parameters from the measured P-E plot. The extracted parameters for the organic ferroelectric material, P(VDF$_{0.75}$-TrFE$_{0.25}$), are as follows:

$$\alpha = \alpha_0 \left(T - T_c \right), \ \alpha_0 = 1.20 \times 10^{11} Jm/C^2 K,$$
$$T = 300K, \ T_c = 413K, \ \beta = 1.20 \times 10^{24} Jm^5/C^4, \ \gamma = 0$$

where T is the room temperature and T_c is the Curie temperature for P(VDF$_{0.75}$-TrFE$_{0.25}$) [19].

$$C_{FE} = \left[\frac{d^2U}{dP^2} \right]^{-1} = \frac{1}{2\alpha + 12\beta P^2 + 30\gamma P^4} \tag{4}$$

From Eq. (1), the capacitance of the ferroelectric capacitor (C_{FE}) can be derived [see Eq. (4)]. For a dielectric capacitor, the static terms (α, β, γ) are positive. Hence, the capacitance of the dielectric capacitor cannot become negative. However, the coefficient α for the ferroelectric material is inversely proportional to the permittivity, $\varepsilon \propto 1/\alpha_0(T - T_c)$, where $1/\alpha_0$ is the Curie-Weiss constant [7]. Thus, it can be negative at sub-Curie temperatures (T_c). Therefore, the Gibb's free energy with the extracted α, β, and γ constants above has two minimum-polarization states. This indicates that to observe the negative differential capacitance, one polarization state must switch to the other polarization state. This state-to-state transition can be activated by applying an external electric field higher than the coercive electric field. While a certain polarization state is switching to the other state, the existence of negative differential capacitance can be experimentally confirmed. Technically speaking, the phase transition of the molecular chains of the P(VDF$_{0.75}$-TrFE$_{0.25}$) is required to directly observe/measure the negative capacitance.

To explicitly measure the negative capacitance, an externally applied voltage higher than the coercive voltage (= coercive electric field multiplied by the thickness of the organic ferroelectric capacitor) should be applied. Since the measured coercive voltages are approximately −0.9 V and 1.2 V [see Fig. 1c], a 200-Hz square-wave voltage [herein, peak-to-peak voltage (V_{PP}) = 16V] was applied for 10 seconds as the source voltage in the circuit.
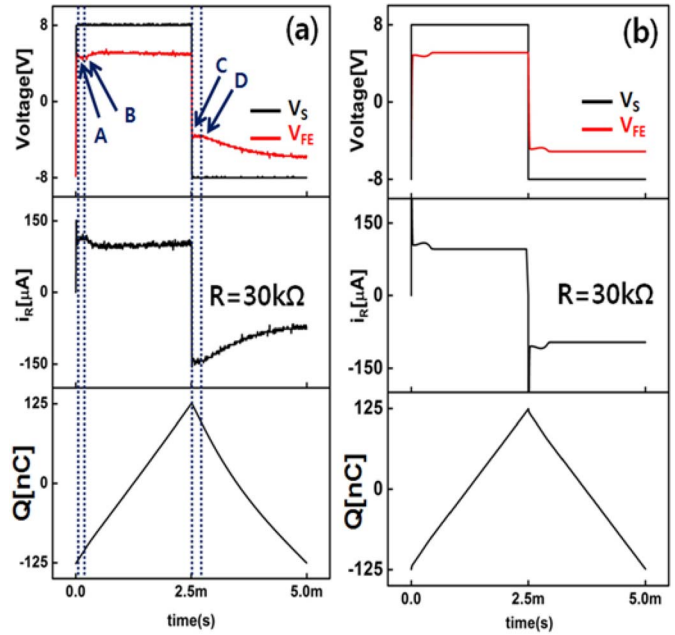

FIGURE 3. (a) Measured transient response of the R-C$_{FE}$ circuit, which explicitly demonstrates the existence of negative capacitance. (b) Simulated transient response of the R-C$_{FE}$ circuit based on the L-K equation with the extracted parameters. Note that V$_S$, V$_{FE}$, i$_R$, and Q are the source voltage, the voltage across the ferroelectric capacitor, the current through R, and the charge, respectively. ρ is taken as 850 kΩ.

Then, the applied source voltage and one cycle of voltage across the ferroelectric capacitor (V$_{FE}$) were directly measured by a Tektronix TDS 2012C oscilloscope. During the 2000 cycles, there was no considerable change of the negative capacitance duration.

The transient response of negative capacitance in the RC circuit is shown in Fig. 3a. Moreover, the current through the external resistor (i$_R$) was directly measured to calculate the total charge as a function of time, i.e., $Q(t) = \int_0^t i_R(t)dt$. Since the capacitance of the organic ferroelectric capacitor (C_{FE}) is $dQ(t)/dV_{FE}(t)$, sections "AB" and "CD" in Fig. 3a show the negative capacitance regions. In section AB, V$_{FE}$ decreases while Q increases. Likewise, V$_{FE}$ increases while Q decreases in section CD. These experimental results apparently indicate that dQ and dV$_{FE}$ have opposite signs.

Although the calculated current exceeds the polarization switching current at the frequency of 200Hz, it clearly demonstrates the negative capacitance regions. Also, it can be expected that the effect of parasitic capacitance would be small because the charge stored in the parasitic capacitance would be negligible due to the leakage charge. It is interesting to note that even though there is a substantial leakage due to the low frequency of source voltage in Figs. 3, 4, 5, the time duration of NC can be still observed. Since the coercive voltages are not symmetric (i.e., −0.9 V and 1.2 V), section AB shows a relatively shorter time duration of negative capacitance than section CD. Because of the difference in negative capacitance time duration, the
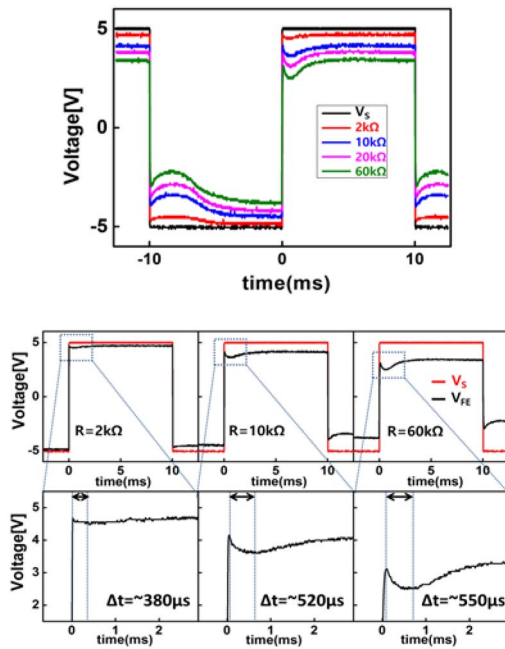
FIGURE 4. Transient responses of R-C$_{FE}$ circuit with various external resistors at 300 K. The frequency of the source voltage is 50Hz.

FIGURE 5. Transient responses at various temperatures. The external resistor is fixed at 30kΩ. The frequency of the source voltage is 50Hz.

amount of charge in the organic ferroelectric material is not identical in both sections, resulting in different internal voltage gains [depending on the gate voltage sweep directions (i.e., forward or reverse)] in a negative capacitance field-effect transistor (NCFET) [2]. Moreover, the imperfect charging behavior of the ferroelectric capacitor in Fig. 3 can be explained by the voltage drop due to the internal resistance of the ferroelectric layer and on the electrodes' interface.

A circuit level simulation with the extracted parameters using the L-K equation [Eq. (3)] is shown in Fig. 3(b). For simplicity, it was assumed that the coercive voltages of the extracted parameters from the Fig. 2 are symmetric (i.e., ±1.1V), and thereby, the turn-off transient response in the simulation [i.e., the transient response starting from t = 2.5 ms in Fig. 3(b)] is closely fit to the turn-on transient response in Fig. 3(a). Since the total current exceeds the polarization current, the non-linear leakage current (i_L) through the leakage resistance (R_L) is assumed.

To experimentally confirm the impact of the RC$_{FE}$ time constant on the transient response of the RC$_{FE}$ circuit, various values are used for the external resistor R, and the results are summarized in Fig. 4. A 50-Hz square-wave voltage [herein, peak-to-peak voltage (V$_{PP}$) = 10 V] was applied as the source voltage in the RC series circuit. Three different cases show different time durations (Δt) of the negative capacitance: Δt increases from 380 μs to 550 μs when R increases from 2 kΩ to 60 kΩ. Thus, the RC time constant can be tuned as in a normal RC circuit. This tuning affects the negative capacitance duration as well. Because the frequency of the source voltage is fixed at 50 Hz, it is evident
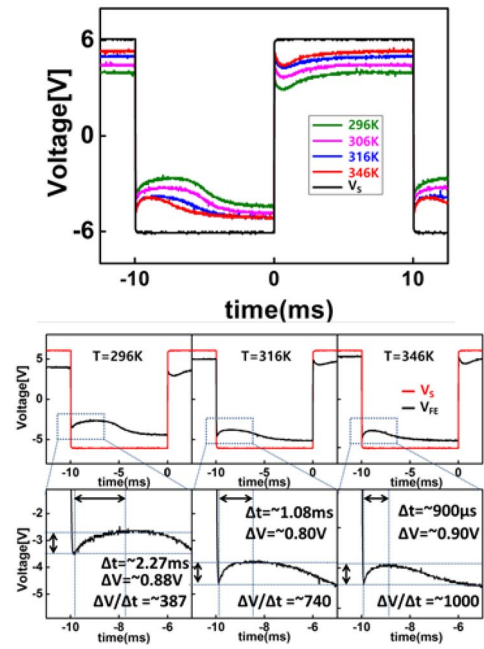
that the organic ferroelectric capacitor is more charged when the RC$_{FE}$ time constant is small, as in a normal RC circuit.

Figure 5 shows the effect of temperature (T) on the negative capacitance duration in the RC$_{FE}$ circuit. Since ferroelectric materials exhibit a phase transition from ferroelectrics to paraelectrics at Curie temperature (T$_c$) or beyond, the ambient temperature is one of the important parameters for evaluating C$_{FE}$[20]. When increasing the temperature up to T$_C$, it can be inferred that α [i.e., $\alpha = \alpha_0$ (T-T$_C$)] reaches to approximately zero while increasing C$_{FE}$ to infinity. Consequently, the NC effect would increase, whereas the NC duration would decrease near T$_C$, according to the Landau's theory [7].

In three different transient responses [see Fig. 5], the time duration (Δt) of the negative capacitance decreases from 2.27ms to 900 μs when T increases from 296 K to 346 K. In order to confirm the temperature dependence of the NC effect, dV$_{FE}$/dt of the NC region is investigated. It is observed that dV$_{FE}$/dt was increased at high T, indicating the increased NC effect. A 50-Hz square-wave voltage [herein, peak-to-peak voltage (V$_{PP}$) = 12 V] was applied as the source voltage in the RC series circuit. This result agrees with the previous experimental results that the internal voltage gain reduces with an increasing temperature in an NCFET using P(VDF$_{0.75}$-TrFE$_{0.25}$) [4], [7]. Therefore, the ambient temperature for an organic ferroelectric capacitor can have impact on the time duration of the negative capacitance.

IV. CONCLUSION
The negative capacitance in an organic ferroelectric capacitor was experimentally and directly observed in an RC$_{FE}$

series circuit. This work demonstrated that the external resistor for the ferroelectric capacitance (C$_{FE}$) could be used as a tuning parameter to control the time duration of the negative capacitance in an organic ferroelectric capacitor. Also, it is shown that the ambient temperature of C$_{FE}$ could alter the time duration of the negative capacitance in the organic ferroelectric capacitor.

REFERENCES

[1] S. Salahuddin and S. Datta, "Use of negative capacitance to provide voltage amplification for low power nanoscale devices," *Nano Lett.*, vol. 8, no. 2, pp. 405–410, 2008, doi: 10.1021/nl071804g.

[2] J. Jo *et al.*, "Negative capacitance in organic/ferroelectric capacitor to implement steep switching MOS devices," *Nano Lett.*, vol. 15, no. 7, pp. 4553–4556, Jul. 2015, doi: 10.1021/acs.nanolett.5b01130.

[3] J. Jo and C. Shin, "Impact of temperature on negative capacitance field effect transistor," *Electron. Lett.*, vol. 51, no. 1, pp. 106–108, Jan. 2015, doi: 10.1049/el.2014.3515.

[4] J. Jo and C. Shin, "Negative capacitance field effect transistor with hysteresis-free sub-60-mV/decade switching," *IEEE Electron Device Lett.*, vol. 37, no. 3, pp. 245–248, Mar. 2016, doi: 10.1109/LED.2016.2523681.

[5] A. Rusu, G. A. Salvatore, D. Jimenez, and A. M. Ionescu, "Metal-ferroelectric-meta-oxide-semiconductor field effect transistor with sub-60 mV/decade subthreshold swing and internal voltage amplification," in *Proc. IEEE Int. Electron Devices Meeting*, San Francisco, CA, USA, Dec. 2010, pp. 1–4, doi: 10.1109/IEDM.2010.5703374.

[6] A. Rusu, G. A. Salvatore, and A. M. Ionescu, "Test structure and method for the experimental investigation of internal voltage amplification and surface potential of ferroelectric MOSFETs," in *Proc. Eur. Solid-State Device Res. Conf.*, Seville, Spain, Sep. 2010, pp. 174–177, doi: 10.1109/ESSDERC.2010.5618400.

[7] G. A. Salvatore, A. Rusu, and A. M. Ionescu, "Experimental confirmation of temperature dependent negative capacitance in ferroelectric field effect transistor," *Appl. Phys. Lett.*, vol. 100, no. 16, pp. 1–4, 2012, doi: 10.1063/1.4704179.

[8] C. H. Cheng and A. Chin, "Low-voltage steep turn-on pMOSFET using ferroelectric high-κ gate dielectric," *IEEE Electron Device Lett.*, vol. 35, no. 2, pp. 274–276, Feb. 2014, doi: 10.1109/LED.2013.2291560.

[9] S. Dasgupta *et al.*, "Sub-kT/q switching in strong inversion in PbZr0.52Ti0.48O3 gated negative capacitance FETs," *IEEE J. Exploratory Solid-State Comput. Devices Circuits*, vol. 1, no. 1, pp. 43–48, Dec. 2015, doi: 10.1109/JXCDC.2015.2448414.

[10] A. I. Khan, C. W. Yeung, C. Hu, and S. Salahuddin, "Ferroelectric negative capacitance MOSFET: Capacitance tuning & antiferroelectric operation," in *Proc. IEEE Int. Electron Devices Meeting*, Washington, DC, USA, Dec. 2011, pp. 1–4, doi: 10.1109/IEDM.2011.6131532.

[11] A. I. Khan *et al.*, "Negative capacitance in short-channel FinFETs externally connected to an epitaxial ferroelectric capacitor," *IEEE Electron Device Lett.*, vol. 37, no. 1, pp. 111–114, Jan. 2016, doi: 10.1109/LED.2015.2501319.

[12] K.-S. Li *et al.*, "Sub-60mV-swing negative-capacitance FinFET without hysteresis," in *Proc. IEEE Int. Electron Devices Meeting*, Washington, DC, USA, Dec. 2015, pp. 1–4, doi: 10.1109/IEDM.2015.7409760.

[13] A. I. Khan *et al.*, "Experimental evidence of ferroelectric negative capacitance in nanoscale heterostructures," *Appl. Phys. Lett.*, vol. 99, no. 11, 2011, Art. no. 113501, doi: 10.1063/1.3634072.

[14] A. I. Khan *et al.*, "Negative capacitance in a ferroelectric capacitor," *Nature Mater.*, vol. 14, no. 2, pp. 182–186, Feb. 2015, doi: 10.1038/nmat4148.

[15] T. Furukawa, Y. Takahashi, and T. Nakajima, "Recent advances in ferroelectric polymer thin films for memory applications," *Current Appl. Phys.*, vol. 10, no. 1, pp. e62–e67, Jan. 2010, doi: 10.1016/j.cap.2009.12.015.

[16] K. Lau, Y. Liu, H. Chen, and R. L. Withers, "Effect of annealing temperature on the morphology and piezoresponse characterisation of poly(vinylidene fluoride-trifluoroethylene) films via scanning probe microscopy," *Adv. Condens. Matter Phys.*, vol. 2013, pp. 1–5, Sep. 2013, doi: 10.1155/2013/435938.

[17] D. Mao, M. A. Quevedo-Lopez, H. Stiegler, B. E. Gnade, and H. N. Alshareef, "Optimization of poly(vinylidene fluoride-trifluoroethylene) films as non-volatile memory for flexible electronics," *Org. Electron.*, vol. 11, no. 5, pp. 925–932, Feb. 2010, doi: 10.1016/j.orgel.2010.02.012.

[18] F. Xia and Q. M. Zhang, "Schottky emission at the metal polymer interface and its effect on the polarization switching of ferroelectric poly(vinylidenefluoride-trifluoroethylene) copolymer thin films," *Appl. Phys. Lett.*, vol. 85, no. 10, pp. 1719–1721, Sep. 2004, doi: 10.1063/1.786364.

[19] V. Sencadas, S. Lanceros-Mendez, and J. F. Mano, "Thermal characterization of a vinylidene fluoride-trifluoroethylene (75–25) (%mol) copolymer film," *J. Non-Cryst. Solids*, vol. 352, nos. 50–51, pp. 5376–5381, 2006, doi: 10.1016/j.jnoncrysol.2006.08.025.

[20] M. Ye *et al.*, "Temperature-dependent reversible and irreversible processes in Nb-doped PbZrO$_3$ relaxor ferroelectric thin films," *Appl. Phys. Lett.*, vol. 107, no. 20, pp. 1–5, Nov. 2015, doi: 10.1063/1.4935951.

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