On the scaling behavior of organic ferroelectric copolymer PVDF-TrFE for memory application

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**Abstract**

We report an interesting scaling trend in the switching time and the switching voltage of the organic ferroelectric copolymer PVDF-TrFE as a function of the device area. We have found that shrinking the lateral dimensions of the ferroelectric film results in a dramatic decrease in the switching time and the switching voltage. The phenomenological theory, that explains this abnormal scaling trend, involves in-plane interaction of the polymeric chains of the two-dimensional Langmuir–Blodgett (LB) films of the copolymer PVDF-TrFE interchain and intrachain coupling results in a weak power-law dependence of the switching field on the device area ($E_{SW} \propto A_{0}^{1/3}$) which is ultimately responsible for the decrease in the switching time and switching voltage. For this scaling study we have used the organic ferroelectric copolymer as the top gate dielectric of a field-effect transistor structure with poly silicon nanowires as channel material. The gated channel area was varied by more than two orders of magnitude (0.04 –5 $\mu$m$^2$) while the thickness of the ferroelectric copolymer film was kept constant at 100 nm. Our findings are believed to be of importance to both, the fundamental understanding of non-equilibrium processes in correlated condensed matter systems and the technological use of ferroelectric copolymers for non volatile memory applications.

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**1. Introduction**

Ferroelectric materials [1,2] are characterized by two stable spontaneous polarization states which can be switched by an appropriate external electric field. These materials are therefore an excellent choice for binary code based nonvolatile random access memory (NVRAM) applications [3,4]. The organic ferroelectric copolymer polyvinylidene-di-fluoride-tri-fluoro-ethylene (PVDF-TrFE) [5–11] has attracted a considerable amount of attention in this context for next generation NVRAM technologies due to its excellent processability, low annealing temperature and tremendous flexibility. Organic copolymers can be integrated with both conventional CMOS technology and emerging organic material based microelectronic technology. However the major road block in the realization of PVDF based NVRAM lies in the high switching voltage of this material. The switching voltage for any ferroelectric material is the product of the switching field and the thickness of the ferroelectric layer. Thus, the switching voltage can be reduced by scaling the thickness of the ferroelectric layer. However, the switching field ($E_{SW}$) itself scales inverse with the thickness ($E_{SW} \propto t_{ox}^{-2/3}$) [12,13] making it extremely difficult to scale down the switching voltage ($V_{SW} = E_{SW} t_{ox} = \gamma^{-1/3}$, $\gamma$ being constant) just by reducing the thickness of the ferroelectric layer. Through our experiments we have found that the switching voltage for a 100 nm copolymer film is around 15 V and therefore 5 V operation would require a 4 nm ultra-thin copolymer film using the thickness scaling law of the switching voltage mentioned above. Controlling the leakage current density and surface roughness of such an ultra-thin copolymer film can be expected to be extremely demanding. In this article we will discuss our findings that indicate an alternative route to reduce the required switching voltage, namely...
by shrinking the gated device area. Our experimental data suggest that the switching field ($E_{SW}$) for the ferroelectric copolymer PVDF-TrFE scales as a function of the device area ($E_{SW} \propto A^{0.1}_{CH}$) and thereby allows to reduce the switching voltage at a given oxide thickness. The origin of such an abnormal scaling trend lies according to our phenomenological theory in the long range interchain and intrachain interaction of the polymeric chains of the two dimensional Langmuir–Blodgett (LB) films of the copolymer PVDF-TrFE [14–16]. Moreover, we conclude from the experimentally found rather large switching times of 500 ns even for the smallest device dimensions (200 nm × 200 nm) that the switching process involves domain nucleation rather than domain wall motion [17,18].

The fabrication process flow for the ferroelectric nanowire transistor is shown in Fig. 1. Photo resist PMMA A4 was spun onto a highly doped silicon substrate with 100 nm silicon dioxide (SiO$_2$) as top layer. The channel length ($L_{CH}$) and width ($W_{CH}$) was then defined by electron beam (e-beam) lithography (Fig. 1a). Amorphous silicon was deposited using e-beam evaporation followed by acetone lift-off to create silicon nanowires of various dimensions. The amorphous silicon nanowires were annealed in a forming gas environment at 950 °C for 10 h for conversion into poly-silicon. Nickel was e-beam evaporated as source and drain contacts after patterning of the contact area by e-beam lithography (Fig. 1b). Organic ferroelectric copolymer PVDF-TrFE (80:20) pellets, were dissolved in methyl-ethyl ketone (MEK) solution (PVDF-TrFE was 2% by volume) and the liquid was then spun onto the sample at 4500 rpm to produce a 100 nm ferroelectric film. By adjusting either the composition of the solution or the spin speed, the thickness of the copolymer layer can be adjusted. Finally, a stack of 20 nm aluminum and 80 nm titanium was deposited to create the top gate for the transistor. Fluorinated plasma was used to etch the metal stack at a rate of 30 nm/min and oxygen plasma was employed to remove the copolymer at a rate of 120 nm/min (Fig. 1c). An SEM image of a readily fabricated device and its cartoon projection are depicted in Fig. 2.

The organic ferroelectric copolymer gated poly silicon nanowire transistors used for the characterization have variable gated channel lengths ($L_{CH}$: 200 – 5000 nm) and widths ($W_{CH}$: 200 – 1000 nm) and hence gated channel areas that vary by more than two orders of magnitude ($A_{CH}$: 0.04 – 5 µm$^2$). The transfer characteristics of a 200 nm long and 200 nm wide nanowire transistor with 100 nm thick copolymer film are shown in Fig. 3a. A back gate bias of +20 V was used to adjust the threshold voltage through electrostatic doping of the nanowire. Note that while this back gate bias impacts the ferroelectric state, the stronger coupling of the top gate still allows changing the polarization of the ferroelectric according to the applied top gate voltage. When the top gate voltage is positive (negative) 20 V the dipoles in the ferroelectric are polarized in the upward (downward) direction which we refer to as binary state “1” ("0") (see simplified band diagrams in Fig. 3b). When the top gate bias is subsequently removed ($V_{GS} = 0$ V), the energy bands in the channel tend to readjust towards their original equilibrium positions, however, the polarization charges in the ferroelectric oxide create a residual electric field which prevents this band movement. The exact position of the energy bands is determined by the respective orientation and strength of the polarization dipoles in the ferroelectric gate insulator. Note that the dipole field in the ferroelectric is ultimately responsible for the non-volatility of ferroelectric based random access memory transistors. Now, since the source to drain current is determined by the position of the bands in the channel region, its amplitude depends on the polarization state of the ferroelectric. The inset of Fig. 3a shows the desired transfer characteristics of such a ferroelectric material based memory transistor. When the transistor is put into binary state “1” (green triangle), the polarization of the ferroelectric ensures that the conduction band of the channel material lies below the source and drain Fermi levels, thereby allowing current to flow from the source to the drain. However if the transistor is put into binary state “0” (blue rectangle), the polarization of the ferroelectric ensures that the conduction band of the channel material lies above the source and drain Fermi levels and prevents substantial current flow from the source to the drain (see also simplified band diagrams in Fig. 3b).

Note that the polarization state of the ferroelectric can be determined simply by reading the magnitude of the current through the channel of the transistor. This read-out process is non-destructive as long as the drain voltage is not too large to depolarize the ferroelectric and provides significant advantages over traditional FeRAM [8,19,20], utilizing ferroelectric capacitors, where the data needs to be rewritten after every read operation.

### Fig. 1. Fabrication steps for the ferroelectric copolymer gated buried poly-silicon nanowire transistor. (a) Channel length and channel width patterning using e-beam lithography. (b) Amorphous Si deposition, conversion into poly silicon through forming gas annealing and source/drain contact formation. (c) Spinning of the copolymer PVDF-TrFE and top gate patterning.
Fig. 2. SEM images and 3-D cartoon projection of a copolymer gated poly-silicon nanowire transistor. (a) Source/drain contacts to the nanowire. (b) The completed transistor with copolymer as top gate dielectric.

Fig. 3. (a) Transfer characteristics of the copolymer gated silicon nanowire transistor (inset shows the ideal transfer characteristics desired for memory application). (b) Energy band diagram for the same transistor at different operating states.

Fig. 4a illustrates the measurement technique employed next to determine the switching time of the ferroelectric copolymer and Fig. 4b shows the corresponding experimental data for a 200 nm long and 200 nm wide nanowire channel transistor. In our approach, every time a set of two pulses was applied – the reference pulse in this technique has a constant amplitude of \(-20\) V for \(t_{\text{Reset}} = 10\) s while the test pulse also has a constant amplitude equal to 20 V but a variable pulse duration. The reference pulse resets the polarization state of the ferroelectric copolymer and hence the source to drain current to a low value. When the pulse duration of the test pulse is less than the switching time of the ferroelectric copolymer, the source to drain current remains the same as the reference current level, however, if the pulse duration of the test pulse becomes more than the switching time, the source to drain current increases. The transition point as shown in the measurement data in Fig. 4b determines the switching time for the ferroelectric copolymer.\(^1\) (note that the memory ratio determined from Fig. 4b (ratio of current in the two states) is \(-3\) in spite of a current ON/OFF ratio of \(-10\) at \(V_{\text{GS}} = 0\) V in Fig. 3b. This is a direct consequence of threshold voltage shift between the measurements and do not have any effect on the intrinsic properties being investigated in this article) This technique was repeated for all devices and the switching time was plotted as a function of the channel length for different channel widths as shown in Fig. 4c. Interestingly both, a reduction in channel width as

\(^1\) The time constant of the measurement setup was 10 ns (much smaller than the lowest switching time) and hence does not limit the switching time. The data, therefore, represents intrinsic properties of the ferroelectric.
well as channel length decrease the switching time. In fact, plotting $t_{SW}$ as a function of gated channel area (Fig. 4d) reveals a clear trend – i.e. increasing the device area ($A_{CH} = L_{CH} W_{CH}$) results in an increase in the switching time (see footnote 1). To explain our experimental findings we are proposing the following phenomenological model:

The switching process for any ferroelectric film involves two steps: nucleation of ferroelectric domains at the metal-ferroelectric interface and growth of these domains through the crystal by domain wall motion. In general it is believed that the nucleation of domains is a statistical process while domain wall motion is controlled by "viscous drag" [23]. The total switching time ($t_{SW}$) can be approximated by the sum of domain nucleation time ($t_n$) and domain wall motion time ($t_d$) [21–23]. It is important to note that at a given field strength the slower of the two mechanisms will determine the switching time. Experimentally it has been observed that the domain walls move at supersonic velocity resulting in a very fast switching (10 ns) even for micrometer thick films [24]. On the contrary nucleation of ferroelectric domains can be a slow process and hence can limit the switching time. The rather large switching time of 500 ns in our 100 nm thin copolymer film, [25], therefore, indicates that the switching process in the copolymer PVDF-TrFE is nucleation dominated [16,26]. The switching time ($t_{SW}$) in such a nucleation dominated process is given by $t_{SW} = t_0 \exp(E_a/E)$, where $t_0$ is a constant, $E_a$ is the activation field which is proportional to the switching/coercive field $E_{SW}$, and $E$ is the applied electric field [20–23]. Since the same electric field $E$ was used to switch the copolymer films in our measurements, the switching time can be expressed as $t_{SW} = t_0 \exp(bE_{SW})$ – according to this argument the switching time only depends on the switching field. With the apparent trend of $t_{SW}$ on channel area according to Fig. 4d, we conclude that $E_{SW}$ in fact exhibits a dependence on $A_{CH}$ [27].

We argue that the Langmuir–Blodgett (LB) films of copolymer PVDF-TrFE are two-dimensional (2D) ferroelectrics comprising of several micrometer long polymeric chains. The electric polarization dipoles in these polymer chains have a limited degree of freedom for rearrangement of charges in that they can rotate only about the chain axis. Moreover, any rotation is further inhibited by both inter-chain steric interaction and intrachain dihedral stiffness [14]. Since switching in our experiments involves the rotation of the chains about the chain axis whereby every molecule reverses local polarization simultaneously, the switching/coercive field required for this process can be...
expected to depend on the area of the film. As the device area is increased more polymeric chains couple with one another and restrict the molecular motion through inter-chain and intrachain interaction. As a consequence of the short and long range in-plane coupling the switching energy and therefore the switching field is expected to increase with the gated device area. The empirical relationship between the switching field and the device area we assume follows a power-law dependence of type $E_{SW} = E_{SW0} A_{CH}^g$. Correspondingly, the switching time for the copolymer can be expressed as $t_{SW} = t_0 \exp(\mu A_{CH}^g)$, with $\mu$ being a constant. In order to fit our experimental data we have used $t_0 = 2$ ns, $\mu = 7$ and $g = 0.1$ ($A_{CH}$ is in $\mu m^2$). The relatively small power exponent $g$ indicates that long range coupling plays a rather small role which is however enhanced in our switching time measurement due to the exponential dependence of $t_{SW}$ on $E_{SW}$.

In order to further support our phenomenological model, we have independently characterized the switching voltage as a function of gated channel region. Fig. 5a illustrates our second measurement approach to determine the switching voltage of the ferroelectric copolymer and Fig. 5b displays the data for a 200 nm long and 200 nm wide nanowire channel transistor with 100 nm copolymer film as gate oxide. Similar to the technique used to determine the switching time of the ferroelectric copolymer, within every cycle a set of two pulses was applied – the reference pulse which has a constant amplitude of $-20$ V and a constant pulse duration of 10 s and the actual test pulse which also exhibits a constant pulse duration of 10 s but at varying amplitude. The reference pulse resets the polarization state of the ferroelectric copolymer and hence the source to drain current (The bottom solid line in Fig. 5b). When the amplitude of the test pulse is less than the switching voltage of the ferroelectric copolymer, the source to drain current becomes distinctly different from the reference current level and is retained for more than 3 h (solid blue line in Fig. 5b). It is important to note that charges in the oxide can also give rise to hysteresis in the transfer characteristics of a transistor. This is why the initial source to

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For interpretation of color in Figs. 5 and 6, the reader is referred to the web version of this article.
channel widths (see Fig. 5c). Evaluating the data systematically determine the switching voltage of the ferro-
indicating that other groups: Othon et al. [26] and Salvatore et al. [28] with our own data, Fig. 4d also shows data reported by two other groups: Othon et al. [26] and Salvatore et al. [28] indicating that $E_{SW}$ follows some universal $A_{CH}$ dependence. The empirical relationship used to fit the experimental data is given by $(E_{SW} = 0.14A_{CH}^{3/2})$ ($E_{SW}$ is in MV/cm and $A_{CH}$ is in $\mu m^2$). It is important to note that the same dependence of $E_{SW}$ on $A_{CH}$ can be used to describe both, our results on the switching time and switching voltage consistently.

Interestingly, a strong dependence of the switching time on ferroelectric film thickness has been reported previously for the copolymer PVDF-TrFE [29]. Interface defects, grain boundaries and even fabrication related conditions can significantly impact the switching kinetics in ferroelectric Langmuir–Blodgett films [30]. Our experimental data show for the first time that the switching kinetics of the copolymer is also affected by the film area, hinting at an anomalous scaling behavior of the switching field as a function of the device area.

Our experimental findings are particularly relevant in the context of nonvolatile memory applications using this copolymer. The switching voltage for any ferroelectric material is the product of switching field and the thickness of the ferroelectric layer. Thus, the switching voltage can be reduced by scaling the thickness of the ferroelectric layer. However, the switching field ($E_{SW}$) scales in an inverse way with the thickness ($E_{SW} \propto t_{ox}^{-2/3}$) making it extremely difficult to scale down the switching voltage ($V_{SW} = E_{SW}t_{ox} = \gamma t_{ox}^{1/3}$, $\gamma$ being constant) just by reducing the thickness of the ferroelectric layer as pointed out above. Fig. 6 shows the switching voltage measured by us corresponding to three different copolymer thicknesses (red crosses) – 60 nm, 80 nm and 100 nm. The channel length and channel width for all of these devices were 4 $\mu m$ and 2 $\mu m$ respectively. The solid red line is a fit based on the above empirical formula for the switching voltage as a function of the thickness of the copolymer film. Following this scaling trend would require scaling of the copolymer thickness to around 5 nm to achieve a switching voltage of $\sim$5 V – a desirable value from a memory standpoint. The leakage current density of such an ultra-thin copolymer film is in most instances unacceptably high. On the other hand, scaling of the switching field and hence the switching voltage with the device area provides a much simpler and more effective way to reach the 5 V operation regime. From our experimental results we conclude that the switching voltage for a 100 nm thick copolymer film can become as low as $\sim$7.7 V when the channel area is aggressively scaled down to $50 \times 50 \mu m^2$ as shown in Fig. 6. Our choice of nanowire is motivated by the fact that the ultra-thin body nature [31,32] of nanowires allows for aggressive channel length and width scaling in the above mentioned context and at the same time miniaturization of device area ultimately results in high memory densities. Utilizing the same scaling trend for the switching voltage as a function of the copolymer thickness at reduced area ($V_{SW} = \gamma t_{ox}^{1/3}$) one can now project a 5 V operation with a copolymer thickness of 30 nm – a ferroelectric film thickness that can easily be realized without gate leakage problems. The switching time for such a scaled device is predicted to be 100 ns. Thus, coupling the scaling of the copolymer film thickness with the scaling of device area may lead to the realization of low voltage and high speed organic ferroelectric memory devices.

In conclusion, we have used a unique characterization technique to study the scaling properties of the ferroelectric copolymer PVDF-TrFE. Our switching voltage and switching time characterization as a function of gated channel region suggest that the switching field of the copolymer scales with the device area. Our findings are relevant in the context of nonvolatile memory applications since scaling the switching voltage is possible without aggressively scaling the copolymer thickness but instead utilizing the area dependence described in this article to tailor the device properties.

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References

[25] The time constant of our measurement setup was evaluated to be 2 ns and as such has no impact on the switching time.
[27] Note that while it is tempting to believe that the switching time (which is the total nucleation time) will increase with the channel area, the larger area will also result in more nucleation processes to occur simultaneously since the nucleation rate per unit area is constant. Thus, for nucleation dominated switching processes, the switching time is expected to be constant as a function of the device area.