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Switching kinetics of ferroelectric polymer nanomesas

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The switching dynamics and switching time of ferroelectric nanomesas grown from the paraelectric phase of ultrathin Langmuir–Blodgett vinylidene fluoride and trifluoroethylene copolymer films are investigated. Ferroelectric nanomesas are created through heat treatment and self-organization and have an average height of 10 nm and an average diameter of 100 nm. Ferroelectric nanomesas are highly crystalline and are in the ferroelectric phase and switch faster than 50 μs. The dependence of switching time on applied voltage implies an extrinsic switching nature. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2975200]

I. INTRODUCTION

The study of polarization dynamics in ferroelectric thin films is highly relevant to both the fundamental study of nonequilibrium processes in correlated condensed matter systems and to the practical application of ferroelectric films to nonvolatile memories, sensors, and transducers. The polarization reversal, or switching, process is usually described by nucleation and domain growth mechanisms analogous to the Kolmogorov–Avrami (KA) theory of phase change dynamics.[1] When applied to ferroelectric thin films,[2,3] KA theory predicts either an activated exponential form depending on both thickness and voltage if nucleation rates limit the process, or a power-law form depending mainly on voltage if domain-wall velocity dominates. It has also been commonly observed that switching dynamics are sensitive to film thickness in a wide range of ferroelectric materials, such as barium titanate,[4] triglycine sulfate,[2,5] and polyvinylidene fluoride copolymers.[6] Though the general trend is that the switching generally becomes slower as film thickness decreases, thickness may not be the most fundamental parameter because of the essential role played by crystal defects, grain boundaries and other nanoscale inhomogeneities,[3,7] which may be qualitatively different for films in different thickness ranges.

The role of defects and grain boundaries in thin films is illustrated by the dependence of switching kinetics on film thickness for copolymers of vinylidene fluoride (VDF) and trifluoroethylene (TrFE), which exhibit switching times ranging from 100 ns in films with thickness on the order of 1 μm made by solvent spinning[8] to over 1000 s in films with thickness on the order of 10 nm made by Langmuir–Blodgett (LB) deposition,[6] a range of 10 decades. It has been proposed that this wide range of switching times is due to the operation of two different mechanisms—extrinsic nucleation and domain-wall propagation in the case of thicker films and correlated intrinsic switching[9] in the case of some LB films, as indicated by the extraordinarily high coercive fields in the LB films that are 15 nm or thinner.[10] The strong dependence of the switching dynamics on film thickness, however, is likely influenced by a qualitative change in film nanostructure,[11,12] which is also sensitive to film thickness and fabrication conditions. For example, differing fabrication conditions produce significant qualitative changes in switching kinetics in the LB films.[6,13] In contrast, the state properties of the ferroelectric copolymers, spontaneous polarization and transition temperature, for example, appear insensitive to film thickness.[14]

The discovery that ferroelectric nanomesas could be made by self-assembly from P(VDF-TrFE) copolymer LB films only a few nanometer thick provides an opportunity to study isolated ferroelectric polymer nanostructures.[15] When the LB films are annealed in the paraelectric phase (in the range of 50–150 °C, depending on composition) without the constraint of a top electrode, they break up and reassemble into circular disks approximately 8–10 nm in height and 50–120 nm in diameter, depending on temperature [see Fig. 1(a)].[16] The nanomesas were found to be highly crystalline, with a *d*-spacing of 0.45 nm, corresponding to the ferroelectric β phase of the bulk copolymer films. They exhibit both a polarization reversal and a paraelectric-ferroelectric phase transition temperature that is only a few degrees lower than in continuous films.[15,16] In the present paper, we report studies of the switching kinetics of the ferroelectric copolymer nanomesas to probe the effect of morphology on switching dynamics.

II. EXPERIMENTAL METHODS

A. Nanomesa film formation and characterization

The samples were layered thin film structures, each consisting of a 0.15 mm thick glass cover slip, an aluminum bottom electrode, a nanomesa film, an insulating film, and an aluminum top electrode, fabricated as follows [see Fig. 1(b)]. The aluminum electrodes, approximately 30 nm thick and 1 mm wide, were deposited by vacuum evaporation through a mask such that the top and bottom stripes were at right angles to each other. The ferroelectric random copolymer consisting of 70% VDF and 30% TrFE (70:30 copolymer) was deposited to the desired thickness by LB deposition, as

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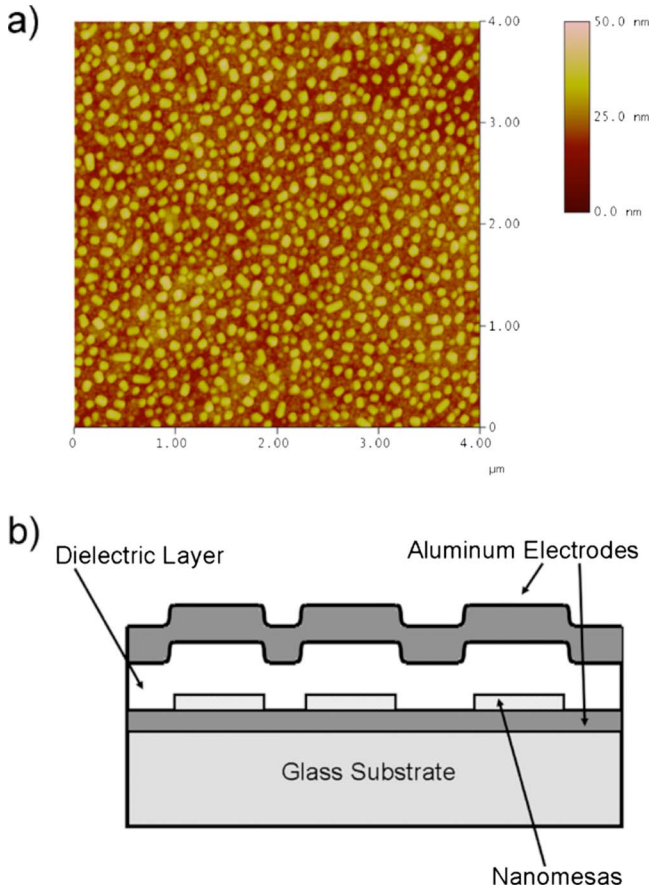

FIG. 1. (Color online) (a) AFM image of a 3-ML P(VDF-TrFE) copolymer nanomesa sample on an aluminum electrode recorded at 25 °C after annealing at 135 °C for 3 h. (b) Sample capacitor diagram illustrating the nanomesas plus an insulating layer.

described in detail elsewhere.[17] Briefly, in this method, a 0.1 wt % copolymer solution in dimethyl sulfoxide was dispersed onto the surface of a subphase of ultrapure (>18 MΩ) water at 25 °C. Barriers on the water's surface slowly compressed the Langmuir film to a surface pressure of 5 mN/m, which was well below the collapse pressure. The copolymer LB films consisting of three nominal monolayers (MLs) were transferred using the horizontal (Schaefer) film method one nominal ML at a time, allowing water droplets to dry completely between transfers. The samples were then annealed at 135 °C for 3 h. Under these conditions the films self-assemble into an irregular array of round, flat mesas approximately 10 nm in height and 100 nm in diameter, as was confirmed by topographical imaging with an atomic force microscope (AFM; Digital Instruments Dimension 3100 in tapping mode at 100 kHz cantilever frequency) as shown in Fig. 1(a). The nanomesas cover approximately $34 \pm 4\%$ of the surface area, leaving roughly $66 \pm 4\%$ of the underlying electrode exposed. All of the nanomesa samples used in these studies were prepared under these conditions.

B. Dielectric insulating layers

To measure the switching characteristics of the nanomesas, it is necessary to deposit a thin insulating film over the nanomesas to prevent the top and bottom electrodes from making electrical contact. For the insulating layers, we chose two materials with high resistivity and high dielectric strength and that could also be deposited using LB deposition so that the thickness was comparable to that of the nanomesas. Polyethylene (PE) has a bulk resistivity on the order of 10^{13} Ω m (Ref. 18) and is not very amphiphilic, but high quality LB films of PE have been made with an average thickness of 5.1 nm per transfer, corresponding to one nominal ML and dielectric strength of approximately 200 MV/m.[19] The PE LB films were prepared from a solution of 0.01% by weight of medium-density PE (0.940 g/cm^3, Sigma-Aldrich) in benzene, dispersed onto a water subphase at 25 °C, and compressed to 10 mN/m. Films consisting of three or four nominal MLs were deposited by horizontal transfer to the substrate, allowing water droplets to dry completely between transfers. One drawback of PE is the low melting point of approximately 110 °C, thus preventing studies of the nanomesa properties near or above the ferroelectric-paraelectric transition temperature of approximately 110 °C.[16] Being a good amphiphile, poly(styrene-co-maleic anhydride) (PSMA) 50:50 copolymer makes excellent LB films.[20,21] With a resistivity on the order of 10^{13} Ω m (Ref. 22) and a much higher melting point above 185 °C,[20] PSMA is a suitable insulating layer for studies near the transition temperature of the nanomesas. The LB films from cumene-terminated PSMA (Sigma-Aldrich, weight-averaged molecular weight MW=1600) were prepared from a solution of 0.1 mg/ml concentration in ethyl acetate dispersed onto a water subphase adjusted with 2.5 μM HCl to *p*H 5.7 at 25 °C and compressed to 30 mN/m. The LB films made by vertical "Y-type" transfer of 3 ML had a resistance of 15 MΩ and a specific capacitance of 2×10^6 nF/mm^3. Assuming a dielectric constant of 3.3,[23] this indicates a total thickness of 3.6 nm, which is in accordance with the literature.[20]

C. Film characterization and polarization switching measurements

Measurements of the capacitance and dielectric loss were made with an ac capacitance meter (Hewlett-Packard 4192A) at a frequency of 1 kHz and an amplitude of 0.1 V. The steady-state pyroelectric response, which is proportional to the net sample polarization,[24] was measured by the Chynoweth optical modulation method,[25] in which the sample was illuminated by a 5 mW He–Ne laser beam, modulated at a frequency of 2 kHz by an optical chopper. The resulting ac current from the sample was measured by a lock-in amplifier (Stanford Research Systems SR850) synchronized with the chopper. To record the polarization hysteresis loops, an electrical bias voltage was applied to the sample for 1 min. Then the bias was removed and the sample was connected to the current inputs of the lock-in analyzer. The sample was illuminated with the modulated laser beam and the resulting ac pyroelectric current measured at zero voltage by the lock-in and allowed to stabilize for 30 s. This was repeated as the applied voltage was cycled stepwise. All measurements were made at 25 °C unless stated otherwise.

The sample switching time as a function of voltage was determined from the current response to a series of switching pulses, two positive pulses in quick succession followed by

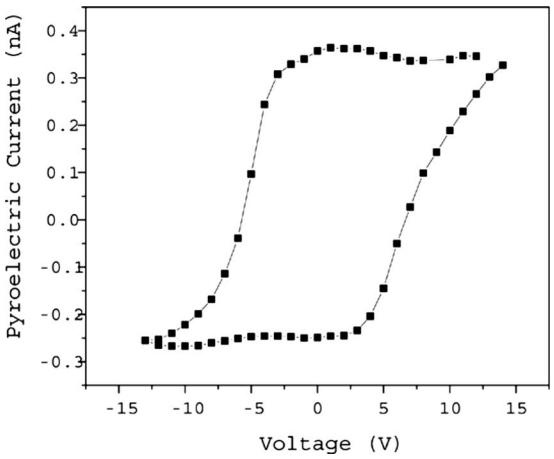

FIG. 2. Pyroelectric hysteresis loop recorded at 25 °C with a nanomesa sample made from a 3-ML P(VDF-TrFE) LB film and a 3-ML PE insulating film.

two negative pulses, all with the same voltage amplitude. The pulses were generated by a Stanford Research Systems DSP345 programmable function generator. The sample current was determined from the voltage across a load resistor connected in series to the sample. The current measured from the first pulse of a pair has two contributions, the displacement current from the capacitor and the polarization switching current, while the second has only the displacement current.

III. RESULTS AND DISCUSSION

Polarization switching is evident with the nanomesa samples as illustrated by the pyroelectric hysteresis loop, shown in Fig. 2, for a nanomesa sample with a 4-ML PE insulating layer. The hysteresis loop exhibits good saturation with an effective coercive voltage of 6.2 V, equal to the half-width of the hysteresis loop at zero pyroelectric current. Because of the insulating layer, the voltage drop across the nanomesas is less than the applied voltage. For this sample, the applied voltage is divided between the nanomesas, which have a thickness of 10 nm and a dielectric constant of 10,[15,26] and the PE film, which should have a thickness of 15.3 nm and a dielectric constant of 2.3.[19] Given these parameters the voltage across each nanomesa was determined to be 0.13 times the applied voltage. (The corresponding voltage division factor was 0.48 for nanomesa samples with 3-ML PSMA insulating layers.) The average coercive field of for this sample was therefore approximately 80 MV/m, much lower than the coercive field obtained from continuous LB films 10 nm thick[10] but comparable to the coercive field obtained in much thicker solvent-crystallized films.[11] The low coercive field indicates that the switching process is extrinsic, proceeding by nucleation and domain-wall propagation, and therefore potentially fast—on the order of microseconds.[8]

The switching time and switched polarization depended on both the amplitude and the duration of the switching pulses. The switching transients of ferroelectric nanomesas were investigated using double-pulse measurements. In the double-pulse method, the sample polarization is switched by

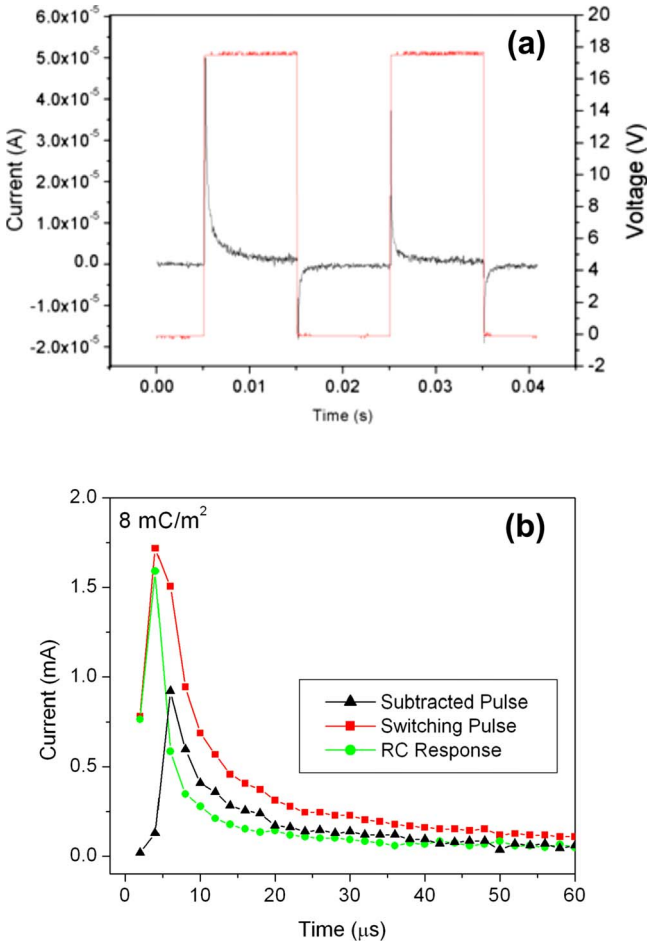

FIG. 3. (Color online) (a) Double-pulse measurements recorded at 25 °C with a nanomesa sample made from a 3-ML P(VDF-TrFE) copolymer film and a 3-ML PE film: the applied voltage (square pulse) and current transient (spiked pulse). (b) Double-pulse measurements recorded at 25 °C with a nanomesa sample made from a 3-ML copolymer LB film and a 3-ML PSMA film. The applied voltage pulses for this measurement had an amplitude of 10 V and a duration of 400 μs and were separated by a 400 μs delay.

the application of a voltage train consisting of two identical voltage pulses followed by two pulses of opposite polarity as shown in Fig. 3(a). The current measured during the two switching pulses has two contributions, the displacement current from the capacitor and the polarization switching current. If polarization switching is completed during the first pulse, then the second pulse contains only the *RC* contribution. Therefore, the polarization switching current transient can be obtained by subtracting the two pulses, as illustrated in Fig. 3(b). Switching pulses with amplitude of 10 V and duration of 400 μs were applied to a nanomesa sample with a 3-ML cumene-PSMA insulating layer. In this case, the subtracted pulse shows a peak in switching current at 4 μs and a switched charge of 8 $\mathrm{mC/m^2}$ (24 ± 3 $\mathrm{mC/m^2}$ when adjusted for nanomesa coverage). A maximum switched polarization of 30 $\mathrm{mC/m^2}$ was measured using the double-pulse method with a switching time below 50 μs. However this measurement was made on a nanomesa sample with a 4-ML PE insulating layer, and the switching peak coincided with the *RC* peak adding some uncertainty to the switching time. When adjusted for the $64 \pm 4\%$ fractional nanomesa coverage obtained from a 3-ML LB film, this corresponds to a true

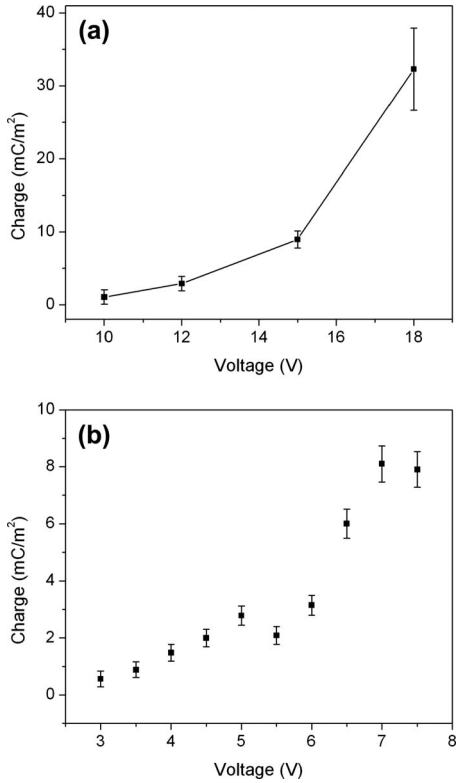

FIG. 4. Switched charge from 3-ML P(VDF-TrFE) copolymer nanomesa samples as a function of the switching voltage recorded by the double-pulse method with at 25 °C. (a) Nanomesa sample with a 4-ML PE insulating film recorded with 5 ms duration pulses. (b) Nanomesa sample with a 3-ML PSMA insulating film recorded with pulses of 400 μs duration.

switched charge of 88 ± 10 mC/m^2, which is approximately half of the maximum expected from complete switching of a saturated film.[27] The values compare well to the conventional LB ferroelectric copolymer films. The smallest observed switching time of 2 μs was achieved for a nanomesa sample with a 3-ML PSMA insulating layer. However only a small fraction of polarization of 4.2 mC/m^2 (12 ± 1.5 mC/m^2 adjusted for coverage) was switching quickly. The electrical breakdown voltage of the insulating layers prevented us from achieving saturated switching of the nanomesas with the short voltage pulses, so that the switched polarization measurements are lower limits only. The ferroelectric LB films[6,10] and ferroelectric nanomesa films[15] generally exhibit symmetric switching characteristics. To test this, we recorded double-pulse switching transients with both positive and negative pulse pairs using half of the samples. We found that the switched charge was symmetric to within 5%.

The dependence of switched charge on switching voltage is shown in Fig. 4 for nanomesa samples with both insulating layers. The switched charge increases steadily with increased voltage. Even with the longer voltage application times, the majority of switched charge occurred in the first 50 μs with the PE insulating layers. There is, however, evidence of prolonged switching in nanomesa samples with the PSMA insulating layer, which achieved up to 20 mC/m^2 (59 ± 7 mC/m^2 adjusted for coverage) with switching pulses of 20 ms duration. The inability to saturate the nanomesa samples, combined with a distribution of switching speeds

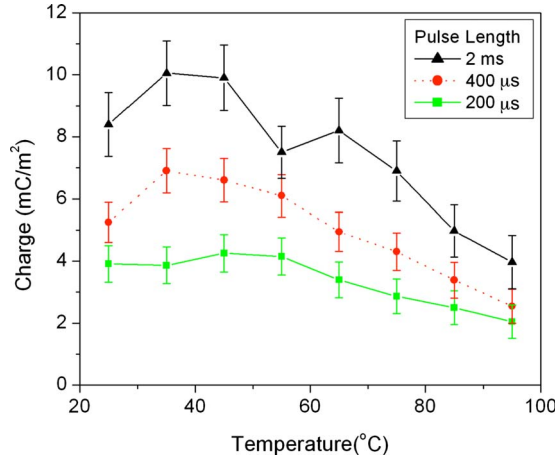

FIG. 5. (Color online) Switched charge from a nanomesa sample made from a 3-ML copolymer LB film and a 3-ML PSMA insulating film as a function of temperature with pulses of 6 V amplitude and pulse duration of 200 μs, 400 μs, or 2 ms as indicated.

for the nanomesa crystallites, makes the interpretation and determination of an absolute switching time ambiguous.

The switched polarization also depends on temperature, as shown in Fig. 5 for a nanomesa sample with a PSMA insulating layer. The switched charge increases slightly up to 40 °C then decreases steadily at higher temperatures. The initial increase may be due to the expected decrease in coercive field of the ferroelectric nanomesas,[10] which would result in better saturation. The steady decline is likely due the decrease in polarization as the sample approaches the paraelectric-ferroelectric transition temperature. In addition, PSMA undergoes a glass transition at 63.9 °C,[28] which would complicate the interpretation of these measurements.

The switching speed also depends strongly on the applied voltage. Figure 6 shows the increase in switching speed, the reciprocal of the switching time, as the switching voltage was increased with a nanomesa sample including a 3-ML PSMA insulating layer. The switching time was obtained from the peaks of the subtracted double-pulse measurements such as the ones shown in Fig. 3. The switching rates are shown only for applied voltage of 4 V or above,

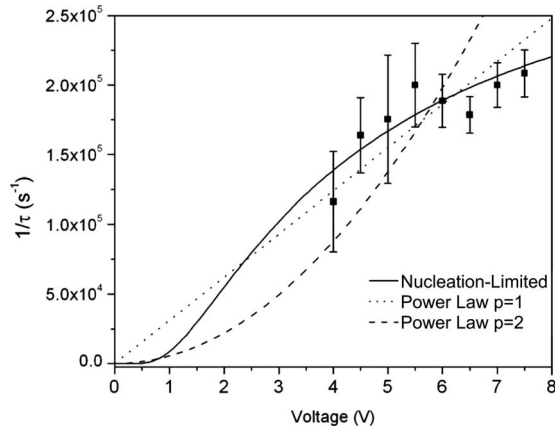

FIG. 6. Reciprocal switching time as a function of applied voltage recorded at 25 °C with a nanomesa sample made from a 3-ML copolymer LB film and 3-ML insulating PSMA film. The voltage pulses were 400 μs in duration.

because lower voltages do not produce sufficient switched charge to show a distinct switching peak. The data in Fig. 6 show clearly that the switching speed increases with voltage but with too much scatter to distinguish among the likely mechanisms. From the lack of an apparent voltage threshold in the switched charge (see Fig. 4) and the relatively short switching time, it appears that intrinsic switching is not important.[6] The extrinsic mechanism of nucleation and domain-wall growth has two clear limits,[2] nucleation-limited switching, which would have an exponential dependence on voltage (solid line in Fig. 6), and domain-wall-limited switching, which would have a power-law dependence (dotted and dashed lines), or some combination of these. Further research is necessary to determine the switching mechanism, particularly studies of the dependence on temperature and nanomesa dimensions and shape.

IV. CONCLUSIONS

In conclusion, we have determined an upper limit in the switching times for nanomesa films of 50 μs, much faster than the switching time of seconds obtained with continuous ferroelectric LB copolymer films of the same thickness. It is possible that the well-defined grain boundaries of the nanomesa films to enable the fast extrinsic switching by nucleation and domain growth mechanism that dominates in thick films consisting of mixed crystalline and amorphous materials. The switching speed and switched charge both increase with increasing switching voltage. The maximum charge switched within 50 μs was 88 ± 10 mC/m^2, about one-fourth of the theoretical maximum. Further study is needed to determine the dominant mechanism of switching in the nanomesa samples. However the fast switching of these samples eliminates the possibility of intrinsic switching in nanomesa films. We expect that there is further opportunity to control polarization switching dynamics in ferroelectric nanomesas through control of nanomesa shape and dimensions. This opens up possibilities to develop high-speed, high-density nonvolatile memory arrays.

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