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COMMUNICATION

Polymer Field-Effect Transistor Memory Based on Ferroelectric Nylon Gate Insulator

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Nylons are one of the most successful commercialized polymers that can also be made to have ferroelectric properties. However, use of nylons in microelectronic devices like ferroelectric field-effect transistors has proven to be challenging due to hardly achievable ferroelectric thin films by solution processing. In this work, we present ferroelectric field-effect transistor (FeFET) memory with a ferroelectric nylon-11 gate. Water quenching allows for the fabrication of ultra-smooth ferroelectric nylon-11 thin film. A bottom-gate top-contact (BGTC) FeFET is successfully demonstrated with a p-type semiconducting polymer, poly(triaryl amine) (PTAA), as a channel. The nylon-11 FeFET shows reliable memory functionality. The demonstration of nylon-11 based FeFETs makes nylons a promising material for applications in organic electronics, such as flexible devices, electronic textiles and biomedical devices.

Introduction

Data storage devices are key components for the upcoming wearable electronics, which requires mechanically flexible materials with reliable electrical memory operation. Ferroelectric polymers have been of great interest owing to their bistable electrical polarization state that gives rise to memory functionality. Memory elements based on diodes, capacitors, flexible and even foldable field-effect transistor (FET) have been demonstrated, using mainly poly(vinylidene fluoride) (PVDF) and its copolymers of poly(vinylidene fluoride-co-trifluoroethylene) (PVDF-TrFE). Despite the availability of various ferroelectric polymers, research is mainly focused on fluoropolymers due to i) ease of processing into thin films and ii) ease of achieving the ferroelectric crystalline phase in thin films upon solution processing.

Polyamides, or nylons, are one of the most successful commercialized polymers and are extensively used in textiles, structural and high performance applications. The polymer chain in nylons is composed of amide units that are separated by CH₂ units. Odd nylons that have an even number of CH₂ units between the amide bonds, exhibit ferroelectric properties i.e. remanent polarization, Pₐ, and coercive filed, Eₓ, that is on par with the fluorinated polymers. Despite their significant potential, microelectronic devices employing odd nylons have rarely been demonstrated, mainly because of difficulty in thin film fabrication of ferroelectric nylons. The exploitation of ferroelectric odd-nylons is hindered due to difficulties associated with i) solution processing of nylons into thin films, and ii) arriving at the crystalline ferroelectric δ-phase, which is characterized by metastable mesophase with randomly oriented hydrogen bonds along the backbone and between the adjacent chains.

Solution processing of nylon thin films is challenging because of the excellent solvent resistance of nylons to most of the common organic solvents. Thin films processed from the limited number of applicable solvents such as formic acid, m-cresol, or trifluoroacetic acid (TFA) produce films with porous structure, which is unsuitable for microelectronic applications. A previous attempt to develop nylon-11 gate insulator using a high boiling point solvent, m-cresol, has resulted in poor memory operation of the comprising FeFETs due to the uncontrolled high roughness of the nylon-11 film. Therefore, nylon-based functional microelectronic devices such as ferroelectric field effect transistors (FeFETs) have hardly been realized.

Recently, we have demonstrated ferroelectricity in solution processed thin films of odd-nylons using solvent mixture of TFA:acetone [60:40 mole percent (mol %)]. The ferroelectric phase is realized by placing the wet spin-coated film in a vacuum chamber to quickly extract the solvent and provide fast crystallization condition. The resulting vacuum-quenched thin
films show small crystallites and absence of a spherulitic superstructures. The solvent-quenching process using vacuum, to some degree, imitates the supercooling process from melt, which is known to yield the pseudohexagonal non-spherulitic δ-phase.21 However, thin films produced by vacuum quenching have roughness of around 5 nm, which is not suited for applications in devices such as FeFETs.22 We hypothesize that the roughness is due to extended solvent-quenching time, since the vacuum is not strong enough to quickly extract solvent molecules. To exactly imitate the supercooling, solvent extraction process should be done much quicker. The δ-phase crystallites are then much smaller and the film roughness would reduce, rendering nylon-11 suitable for FeFET applications.

Here, we report FeFETs based on ultra-smooth nylon-11 thin film that are realized by solvent quenching method using a non-solvent, water. The resulting nylon-11 films are non-porous and show dielectric and ferroelectric properties similar to the vacuum-quenched ones. The resultant nylon FeFETs show excellent memory functionality with an ON-OFF ratio, good retention time and excellent cycle endurance. Our demonstration of nylon FeFET offers a great opportunity for technological utilization of nylon in microelectronics.

Experimental

Materials: Nylon-11 was purchased from Sigma Aldrich. TFA and acetone (99.8%, Extra Dry) were purchased from Carl Roth GmbH and Acros Organics, respectively. PTTA was purchased from Merck. All materials were used as received.

Preparation of Nylon-11 thin films: Nylon-11 was dissolved in TFA:acetone mixture (60:40 mol %) with the concentration of 35 mg ml⁻¹. Thin films were fabricated by spin-coating the solution on glass substrates for one minute at 1000 r.p.m., followed by placing the substrate either in vacuum desiccator (vacuum quenching) for 15 minutes or in deionized water bath (water quenching) for 5 s. The thickness of nylon-11 thin films was around 300 nm.

Device fabrication: To fabricate ferroelectric capacitors, 50 nm Au bottom electrodes with a 1 nm Cr adhesion layer were thermally evaporated using a shadow mask on glass substrates. After forming nylon-11 thin films, Au top electrode (50 nm) was deposited using the shadow mask to form crossbar pattern with the capacitor area of 0.0016 cm². A bottom gate, top contact (BGTC) transistor was fabricated on the glass substrate. For the gate electrode, Cr (1 nm) and Au (50 nm) were deposited by thermal evaporation with a predefined shadow mask. The nylon-11 gate dielectric was formed on the gate electrode by water quenching. PTAA was dissolved in toluene (1 wt%) and spin-coated on top of a nylon film at 1000 r.p.m. for 60 s to form a 70 nm layer. A 30 nm of Au was thermally evaporated onto the PTAA-nylon stack through a shadow mask defining the source and drain electrodes with a channel length of 20 μm. The as-fabricated FeFETs were heated at 80 °C for 2 hours in vacuum oven to remove traces of residual solvents.

Structural characterization: The surface morphology of the resulting thin films was inspected with atomic force microscopy (AFM) (Nanoscope Dimension 3100 Bruker). Wide-angle X-ray diffraction (WAXD) measurements of the films were performed at the DELTA Synchrotron using beamline BL09 with a photon energy of 13 keV (λ = 0.9537 Å). The beam size was 1.0 mm × 0.2 mm (width × height), and samples were irradiated just below the critical angle for total reflection with respect to the incoming X-ray beam (~0.1°). The diffraction intensity was detected on a 2-D image plate (MAR-345) with a pixel size of 150 μm (2300 × 2300 pixels), and the detector was placed 523 mm from the sample center. Diffraction data are expressed as a function of the diffraction vector: q=4π/λ sin(Θ), where Θ is a half the diffraction angle and λ=0.9537 Å is the wavelength of the incident radiation. All X-ray measurements were performed under vacuum (~1 mbar) to reduce air scattering and beam damage to the sample.

Electrical Measurements: Ferroelectric capacitors were characterized in a vacuum probe station at 10⁻⁵ mbar. The D-E hysteresis loops were measured using a Radiant precision multiferroic test system (Radiant Technologies, Inc.). Data retention and polarization fatigue tests were performed using the same setup. For data retention, a write pulse was followed by two read pulses of the same amplitude but opposite direction. All pulse widths were fixed at 10 ms. The fatigue test was performed using a continuous triangular waveform with the amplitude of 250 MV/m. After a predefined number of cycles, the remanent polarization was determined by PUND measurement using 10 ms wide pulses. Impedance measurements were performed as well in vacuum at 10⁻⁵ mbar, using a Novocontrol analyser. Electrical measurements of FeFETs were carried out in vacuum with a Keithley 4200-SCS instrument. Retention of the ON- and OFF current at VGS= −10 V is measured after a single-sweep of VGS from 0 V to −50 V (programming) and +50 V (erasing), respectively. The switching cycle is measured after pulsing −50 V and +50 V for 100 ms to set the FeFET in the ON and OFF states, respectively.

Results and Discussion

Figure 1a and 1b present AFM height and phase images, respectively, for the reference nylon-11 thin film quenched in vacuum. The film is composed of small crystallites and does not show spherulitic microstructure. The film is optically smooth and has a uniform height of ~5 nm. Figure 1c and 1d, on the other hand, show the AFM images of the thin film quenched in water, which exhibit a higher roughness with a RMS value of ~2 nm. The surface morphology of the nylon-11 films is crucial for the electrical properties of the resulting FeFETs. The smoothness of the films can affect the leakage current and the reliability of the device. Therefore, the water quenching process may be more suitable for producing high-quality FeFETs.
transparent, but the mean RMS roughness is around 5 nm. The water-quenched thin film, Figure 1c and 1d, shows the non-spherulitic morphology, same as the one of vacuum-quenched films. However, the water-quenched thin films show remarkably low RMS roughness values around 2 nm.

For solvents that are miscible with water, placing the solvent-wet film in a water bath leads to liquid-liquid (L-L) demixing, resulting in polymer-rich and polymer-poor phases. As a result, a porous and rough morphology is obtained for the solidified film. From this point of view, achieving ultra-smooth films of nylon-11 film. The quick depletion of TFA:acetone from the film mimics supercooling of nylon-11 from the melts, which yields the crystalline ferroelectric $\delta'$-phase.21 Figure 2 shows the WAXD patterns of the water-quenched thin film and, as reference, that of the melt-quenched-stretched (MQS) thick film. The MQS film shows the (001) diffraction peak at 4.79 nm$^{-1}$, corresponding to d-spacing of 1.311 nm in perfect agreement with the literature values of the $\delta'$-phase.13, 24-26 The (001) reflection gives the length of repeat units in the crystalline structure along the polymer chain. A second diffraction peak at 15.10 nm$^{-1}$ (d-spacing of 0.416 nm) is a superposition of the (100) and (010) peaks and gives the inter-chain distance along the hydrogen bonds and the inter-sheet distance between the hydrogen bonded sheets, respectively. Presence of a single diffraction peak around 15 nm$^{-1}$ indicates the low intermolecular arrangement of the chains with random orientation of hydrogen bonds along the backbone and between adjacent chains.10, 14

The diffraction peaks of the water-quenched thin film show similar reflections to that of the MQS thick film, as well as the vacuum quenched one.21 The (001) and (100/010) reflection peaks for water-quenched thin film are exactly at the same position. Therefore, the WAXD measurement unambiguously indicates that water quenching allows to readily produce thin films of nylon-11 with ferroelectric $\delta'$-phase.

Crystallization at high solvent depletion rates is governed by homogeneous nucleation, where the number of nucleation sites upon solidification is several orders of magnitude larger in comparison with crystallization at low solvent depletion rates, such as conventional spin coating. Due to the large number of crystallites, lateral growth of crystalline lamellae into spherulites is hindered, and therefore ferroelectric $\delta'$-phase is obtained.21, 23 The quick depletion of TFA:acetone from the film

![Figure 2. WAXD pattern for water-quenched thin film compared with a melt-quenched stretched thick film.](image-url)

Figure 3. (a) D-E ferroelectric hysteresis loop (top) and switching current (bottom) of vacuum- and water-quenched thin films represented as black and red circles, respectively (b) Cycle endurance and polarization retention of the water-quenched film.
We note that nyons are known for their water uptake. Presence of water molecules inside the film would jeopardize the ferroelectric performance of the nylon-11 capacitor. To investigate whether water uptake takes place during water quenching, we have studied the dielectric response of the nylon-11 thin films. Figure 4 shows relative permittivity, $\varepsilon'$, and loss spectra, $\varepsilon''$, of both vacuum- and water-quenched samples. The $\varepsilon'$ or the dielectric constant exhibits a very weak frequency dependence at low frequency limit $(< 1 \text{Hz})$ which is about 4, and reduces to 3.5 at 1 MHz. The lack of strong frequency dependence, particularly at low frequencies could be assigned to the lack of ions (water or solvent molecules) in the films. The loss for both films is about the same and again shows only weak frequency dependence. The impedance spectra indicate lack of ions, including water molecules, in both films, in particular in the water-quenched nylon-11 film. Therefore, water quenching process has no effect on the performance of the nylon-11 capacitors and does not hinder the application of nylon-11 for microelectronic devices.

Achieving low roughness with minimized dielectric losses renders water-quenched nylon-11 thin films suitable for a gate insulator in FeFETs. To that end, nylon-11 FeFETs with BGTC architecture and p-type semiconductor, polytriazyliamide, PTAA have been fabricated. The device schematic and chemical structure of PTAA are shown in Figure 5a.

The sweeping direction represented by arrow shows ferroelectric switching and resultant hysteresis. Figure 5c shows the current level in the PTAA channel at a read gate voltage of $V_{GS} = 0 \text{ V}$ repetitively changed upon programming at $V_{GS} = -50 \text{ V}$ (ON-state) and erasing at $V_{GS} = +50 \text{ V}$ (OFF-state). The ON-OFF ratio of the PTAA channel current maintained around 30 after switching over 60 times. The switching time for the nylon-11 FeFET is set to 100 ms to provide longer time for polarization at the switching field of 167 MW/m$^2$ ($V_{GS} = 50 \text{ V}$), which is lower than 250 MV/m used in the
capacitor. We note that nylon-11 has shown excellent endurance under repetitive polarization switching cycles for more than 10^6 cycles (Figure 3b). Therefore, upon further switching of the nylon-11 gate, the same ON/OFF ratio is expected.

Conclusions

We have successfully demonstrated that water quenching produces ultra-smooth and pinhole-free ferroelectric nylon-11 films of sub-micron thickness with a low dielectric loss. The resultant nylon-11 film has been used as a gate insulator in BGTC thin film transistors. The ferroelectric nylon gate has allowed us to develop a p-type polymer-based FeFET memory with PTAA as semiconducting polymer channel. The FeFET has shown a high ON-OFF ratio, good data retention time, and reliable cycle endurance. Our result suggest that commercially available, easily synthesized, and cost-effective nylon can be fully exploited in microelectronic devices like thin film transistors and memory.

Conflicts of interest

There are no conflicts to declare.

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