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Tunable Ferroelectricity of Highly Oriented PVDF Homopolymer Ultrathin Films from Relaxor-like Ferroelectrics to Ferroelectrics

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1. Introduction

In ferroelectric memories information is stored via two antiparallel polarization states coded "0" and "1". A long-term endurance of the polarized state, high polarization value as well as low-voltage operation are critical for poly(vinylidene fluoride) (PVDF) based ferroelectric memories. Therefore, a high content of polar crystals is required which attributes to a high remnant polarization value (P_r). In the case of low-voltage operation, miniaturizing the thickness of ferroelectric materials is usually good choice because ferroelectrics switch at a threshold electric field, the coercive field (E_c). However, the decreased crystallinity as well as the low content of polar crystals in PVDF thin films confined their further applications. This technical bottleneck has thus far limited the applications of PVDF homopolymer to micro/nanoelectronics. In addition, fatigue properties of PVDF homopolymer films, especially ultrathin films have not been reported.

In the present study, a series of PVDF ferroelectric nanocapacitors (FeNCs) was fabricated with different film thicknesses from 12 nm to 81 nm (ultrathin film) by LB technique. It was firstly demonstrated that highly oriented PVDF LB ultrathin films without any post-treatment retain robust room-temperature ferroelectricity down to 12 nm by a macroscopic measurement method.

2. Results and discussion

Preparation of PVDF FeNCs

We fabricated a series of FeNCs by sandwiching PVDF LB nanofilms between aluminum (Al) bottom and top electrodes. PVDF LB ultrathin films were transferred from the air-water interface according to our previous report.[1] PVDF LB ultrathin films at different numbers of layers, are termed as 5LB (12 nm), 15LB (35 nm), 25LB (58 nm) and 35LB (81 nm), respectively. Dominant polar crystals (Form I) were investigated in the obtained PVDF LB ultrathin films by FTIR and XRD measurements.

Ferroelectricity of PVDF FeNCs

With the increasing of the layer numbers of PVDF LB ultrathin films from 5LB to 35LB, the hysteresis loops (Figure 1) were measured by a home-made Sawyer-Tower circuit. The hysteresis loop for as-prepared 5LB FeNC is narrow, and shows relaxor-like ferroelectricity with a P_r of 1.7 μC/cm^2. Due to the confinement of substrate surface, a low P_r of 2.0 μC/cm^2 is also obtained in the 15LB FeNC. On the other hand, the P_r value increases to 5.3 and 6.6 μC/cm^2 for 25LB (58 nm) and 35LB (81 nm) FeNCs, respectively, even higher than that reported in PVDF microfilms.[2] Therefore, we conclude that the interfacial effect has a critical length less than 58 nm in the PVDF FeNCs.[3] Moreover, by varying the thickness in the nanoscale, we easily modulated the property of PVDF films from relaxor-like ferroelectric to normal ferroelectric for low-voltage nonvolatile memories.

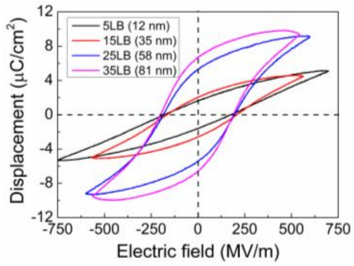

Figure 1. Ferroelectric hysteresis loops of PVDF FeNCs at different layers measured at 10 Hz.

Fatigue properties of PVDF FeNCs

We found that the fatigue properties of PVDF FeNCs are much better than those of copolymers. Mai et al reported that 37-nm PVDF copolymer FeNC shows 47% loss of P_r after 10^6 cycles switching.[4] On the contrary, 5LB FeNCs shows only 22% loss of P_r at 10^6 cycles switching (Figure 2). Moreover, ferroelectricity was kept after 10^7 cycles. The lower fatigue rate in PVDF homopolymer FeNCs may originate from the absence of crystal defects, which are seen in copolymers introduced by the copolymerization repeating unit, such as trifluoroethylene (TrFE).

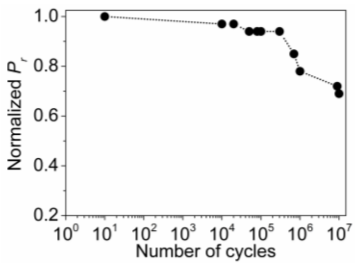

Figure 2. Fatigue property of a 5LB PVDF FeNC measured at 580 MV/m, 100 Hz.

3. Conclusions

In summary, ferroelectricity was firstly detected in an PVDF ultrathin film (5LB, 12 nm). With the increasing thickness, the P_r of PVDF FeNCs showed a sudden increase from 2.0 to 5.3 μC/cm^2, indicating the critical thickness of the interfacial effect less than 58 nm. The ferroelectricity was easily modulated from relaxor-like ferroelectric to normal ferroelectric which make it possible to realize low-voltage operation in FeNCs for nonvolatile memories. Moreover, the long-standing fatigue properties endow the PVDF FeNCs higher performance than that of PVDF copolymer.

References

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