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Ferroelectric Characteristics Enhancement of P(VDF-TrFE) Capacitors with Modified Solvent Vapor Annealing Process

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Abstract

Modified solvent vapor annealing (MSVA) has been demonstrated to enhance the dipole alignment and crystallinity of P(VDF-TrFE) films. With an optimized MSVA, the P(VDF-TrFE) capacitors exhibit superior ferroelectric behaviors including the larger remnant polarization and lower coercive electric field, which are proved by the leakage current and internal bias field (E_{bias}) characterization. The P(VDF-TrFE) films with MSVA technique can be applied in future high-performance nonvolatile memories (NVMs).

1. Introduction

Ferroelectric polymers have attracted much attention due to their applications on flexibility, room-temperature fabrication, low-cost, and simple process [1]. PVDF is one of the most promising one because of the unique advantages such as the good mechanical elasticity, high breakdown electric field, and the ability of self-healing [2]. The ferroelectricity of PVDF and its copolymer P(VDF-TrFE) was proposed by Furukawa in 1980 [3]. P(VDF-TrFE) is a semicrystalline material with α, β, γ and δ phases [4], and its ferroelectric behaviors can be ascribed to the β phase. To increase the ferroelectricity, some studies have proposed to enhance the *β* phase for a highly crystallite structure [5]. In this study, we use a modified solvent vapor annealing (MSVA) treatment on the P(VDF-TrFE) films to reorganize the degree of the crystallinity. The MSVA process is optimized to find the adequate factors of the amount into the P(VDF-TrFE) films, suitable for further high-performance NVM applications.

2. Experimental

The metal-ferroelectric-metal (MFM) capacitors have been fabricated on 4-inch n^+-Si wafers. Initially, the wafers were cleaned by the standard RCA cleaning procedures. Then, the P(VDF-TrFE) powder (70:30 mole %) was dissolved in DMF for 5.0 wt. %, and the solution was spin-coated on Si wafers for three times. The DMF solvent vapor annealing was performed on different layers for 1 - 3 hours at 90 ºC. All samples were annealed at 130 ºC for 2 hours to enhance crystallinity. Finally, a 300-nm-thick Al was deposited by a thermal coater and then defined lithographically and etched. The schematic device structure, process flows, MSVA process, and instructions of samples are shown in Fig. 1. The crystallinity was examined by the X-ray diffraction (XRD) patterns and the polarization versus electric field (*P-E*) hysteresis curves were measured by Keithley 4200-SCS semiconductor characterization system.

3. Results and discussion

Fig. 2 depicts the XRD patterns of the P(VDF-TrFE) films with MSVA. It can be clearly observed that there is a prominent peak at about 20°, indicating the *β* phase of the P(VDF-TrFE) films, especially for the MSVA. The enhanced remnant polarization ($2P_r$) and reduced coercive electric field (E_c) of the samples with MSVA are achieved, as shown in the typical *P-E* characteristics of Fig. 3, due to the crystallinity reorganization. Among the samples, the 3XX sample presents the highest $2P_r$ value because the orientation of dipole becomes orderly at the 1st layer, leading to the best crystallinity of P(VDF-TrFE) film. The extracted values of $2P_r$ and E_c are summarized in the statistical distributions of Fig. 4. Fig. 5 shows the leakage current of all samples. For the samples treated by MSVA on different layers of P(VDF-TrFE), the dipole aligns at different sides of the film, influencing the leakage current accordingly. Fig. 6 presents the distributions of E_c versus E_{bias} of all samples. With the shift of E_{bias} values toward the positive direction, the crystallinity of the P(VDF-TrFE) films with MSVA at 1st layer become more asymmetric [6], which can be illustrated in the schematic mechanism diagrams of MSVA of Fig. 7.

4. Conclusions

In this work, the effects of MSVA on the P(VDF-TrFE) ferroelectric capacitors have been investigated. The XRD patterns proved the better crystallinity of the P(VDF-TrFE) films with MSVA, which can increase the remnant polarization and reduce the coercive electric field of the ferroelectric devices, promising for the applications in future NVMs.

Acknowledgements

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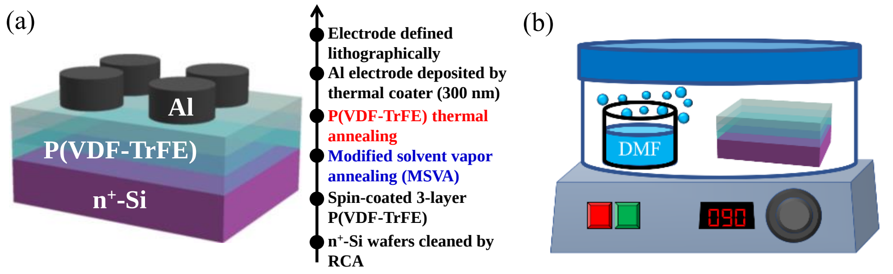

(c)

	XXX	1XX	2XX	3XX	XX1	XX2	XX3	111
Top layer	-	-	-	-	1 hr.	2 hrs.	3 hrs.	1 hr.
Middle layer	-	-	-	-	-	-	-	1 hr.
Bottom layer	-	1 hr.	2 hrs.	3 hrs.	-	-	-	1 hr.

Fig. 1. Schematic of (a) device structure and detailed process flows of P(VDF-TrFE) ferroelectric capacitors with MSVA treatments, (b) MSVA process, and (c) detailed instructions of samples.

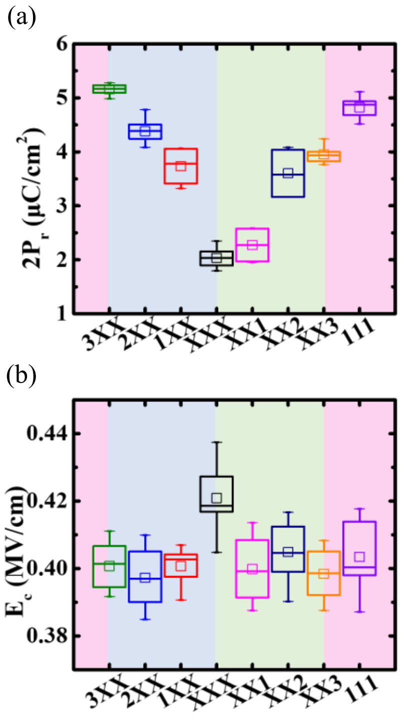

Fig. 4. Statistical distributions of (a) $2P_r$ and (b) E_c of the MSVA-treated P(VDF-TrFE) ferroelectric capacitors. At least 10 devices were measured for each sample.

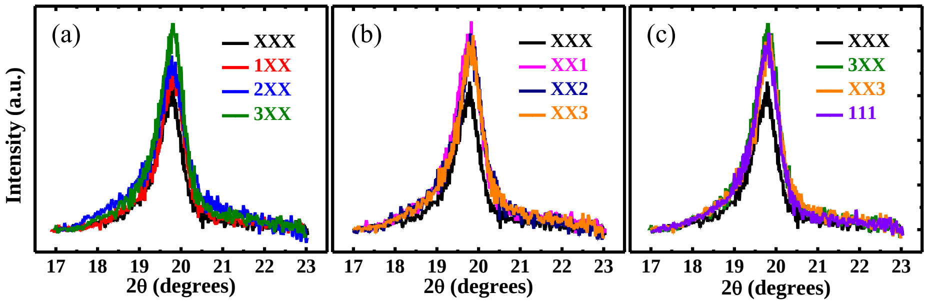

Fig. 2. XRD analysis of P(VDF-TrFE) films with MSVA treatment at (a) the 1st layer, (b) the 3rd layer and (c) total 3 hours. The peak at around 20° indicates the β phase for ferroelectric properties.

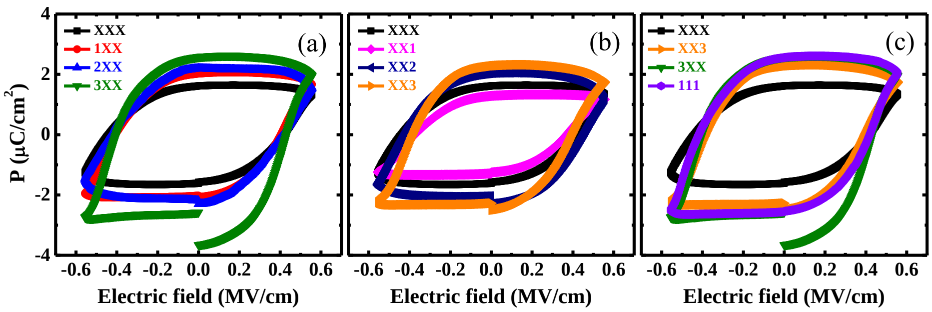

Fig. 3. The *P-E* hysteresis curves of P(VDF-TrFE) ferroelectric capacitors with MSVA treatment at (a) the 1st layer, (b) the 3rd layer and (c) total 3 hours. Significant improvements of MSVA treatments on ferroelectric properties of P(VDF-TrFE) films can be observed.

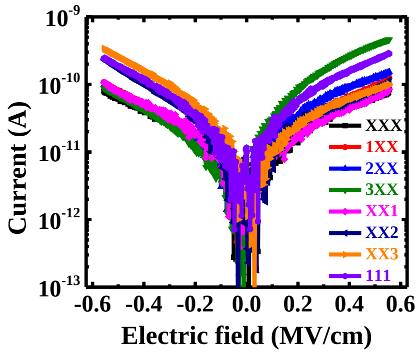

Fig. 5. The leakage current characteristics of the MSVA-treated P(VDF-TrFE) ferroelectric capacitors.

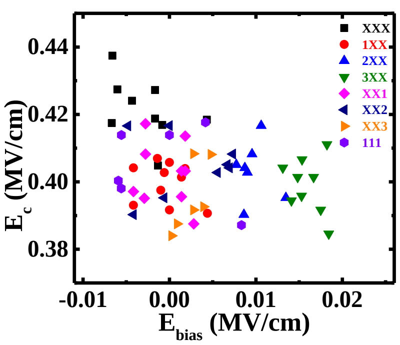

Fig. 6. The distributions of E_c versus E_{bias} for the MSVA-treated P(VDF-TrFE) ferroelectric capacitors.

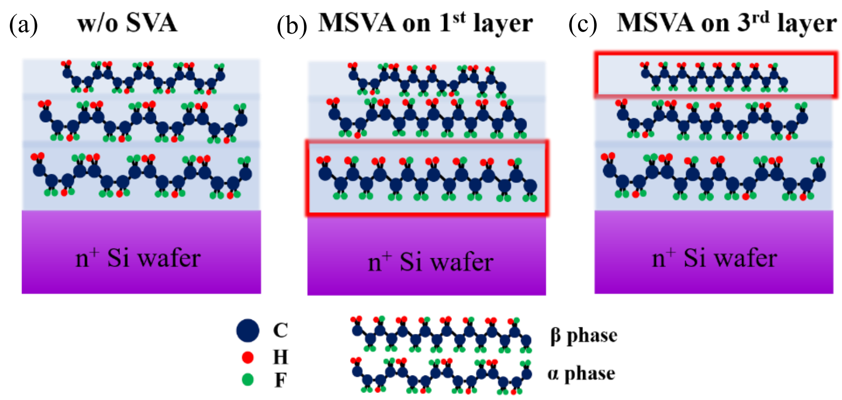

Fig. 7. Schematic mechanism diagrams of the P(VDF-TrFE) films (a) w/o and with MSVA at (b) 1st layer and 3rd layer respectively.