

Effect of Thickness on Electrical Properties of PVDF-TrFE (51/49) Copolymer

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Abstract

In this study, polyvinylidene fluoride-trifluoroethylene (PVDF-TrFE) in the composition from 51/49, was deposited on platinum for a metal-ferroelectric-metal structure. From XRD patterns, the 70 nm- and 140 nm-thick PVDF-TrFE films showed the intensity peak of near 20° connected to a ferroelectric phase. Moreover, the thicker film indicated the higher intensity than thinner one. The difference of the remanent polarization ($2Pr$) at 0 V is decreased gradually from 10.19 to $5.7 \mu\text{C}/\text{cm}^2$ as the thickness decrease from 140 to 70 nm. However, when the thickness decreased to 50 nm, the $2Pr$ rapidly drop to $1.6 \mu\text{C}/\text{cm}^2$ so the minimum critical thickness might be at least 70 nm for device. Both different thickness films, 70 and 140 nm, indicated that the characteristic of current density-voltage was measured for $10^{-6} \sim 10^{-7} \text{ A}/\text{cm}^2$ below 15 V and the thicker film maintained relatively lower current density than thinner one. From these results, we can expect that the electrical properties for the devices particularly ferroelectric thin film transistor using PVDF-TrFE copolymer were able to be on the trade-off relationship between the remanent polarization with the bias voltage and the leakage current.

Key Words : PVDF-TrFE, Ferroelectric, Thickness, FeRAM

1. INTRODUCTION

There has been growing interest in applying organic material to electronic devices such as RF identification tag and organic light-emitting diodes[1]. Among organic materials, Poly(vinylidene fluoride) (PVDF) and its copolymer with trifluoroethylene (PVDF-TrFE) are representative organic dielectrics which have been investigated for a long time[2]. In particular, they have unique ferroelectricity making themselves attracted much attention for nonvolatile memory application[3]. However, PVDF-TrFE copolymers require a very high electric field of 100 MV/m for polarization

reversal. Such a high electric field may not be compatible with many applications such as data storage and memory devices. Therefore, the decrease of the film thickness is a key issue for lower operation voltage. T. Furukawa et al. mentioned that the film thickness should be below 100 nm for establishing low-voltage operation[2]. Some recent researches reported the achievement of the low-voltage operation using PVDF-TrFE copolymers[4,5]. However, there has been no sufficient consideration of the relationship between the film thickness and the ferroelectric property as the film thickness becomes thinner. We present here a study of the ferroelectric properties of PVDF-TrFE films with different thickness having in mind the low-voltage operation.

2. EXPERIMENTS

In this study, the PVDF-TrFE copolymer with

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the composition ratio of 51/49 was chosen. For spin-coating process PVDF-TrFE was dissolved in methylethylketone (MEK) at 65 °C with stirring for 2 hours on a hot-plate. The PVDF-TrFE thin film was deposited on a Pt substrate. The coated film was heat-treated to remove the solvent and improve its crystallization structure. To remove the solvent, drying process was performed at 120 °C on a hot-plate for 10 minutes. The control of the film thickness could be achieved by changing the concentration of the solution and modifying the spin-velocity during the coating process. The film thickness was varied from 50 to 140 nm.

The crystallization of the PVDF-TrFE film was measured by an x-ray diffractometer (XRD) on Rikagu Miniflex. For a metal-ferroelectric-metal (MFM) structure, Au was thermally evaporated onto the surface of the film ($r=100 \mu\text{m}$) for top electrode. The electrical properties of the Au/PVDF-TrFE/Pt/Ti/SiO₂/Si structure are characterized using the Precision LC parameter analyzer on Radiant technology.

3. RESULTS AND DISCUSSION

Figure 1 shows XRD patterns for two PVDF-TrFE films with different film thickness, 70 and 140 nm. Outstanding diffraction peaks near 2θ of 20° could be observed. According to the literature, XRD peak near 20° is concerned with the β -phase among 4 crystallization phases (α , β , γ and δ) the PVDF-TrFE thin film can form[6]. Moreover, the β -phase of crystalline structure is closely related to the ferroelectricity of the thin film[1]. As can be seen in the Fig. 1, the diffraction peak for the thick PVDF-TrFE film was more intense than that of thinner one. In general, thicker films tend to be crystallized more. Figure 1(a), the magnified image near 2θ of 20° revealed that each peak consisted of two point peaks indicating two different phases coexisted in films. The first peak point corresponded to the paraelectric α -phase and the second is related to the ferroelectric β -phase[6]. This result may come from short annealing time

(just 10 minutes). Indeed, the trans-gauche bond (α -phase) was known to be energetically more stable state than the all-trans bond (β -phase)[7].

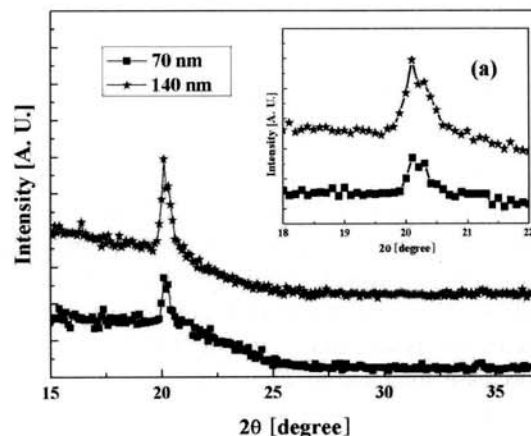


Fig. 1. The XRD patterns of 70 and 140 nm-thick PVDF-TrFE (51/49) films.

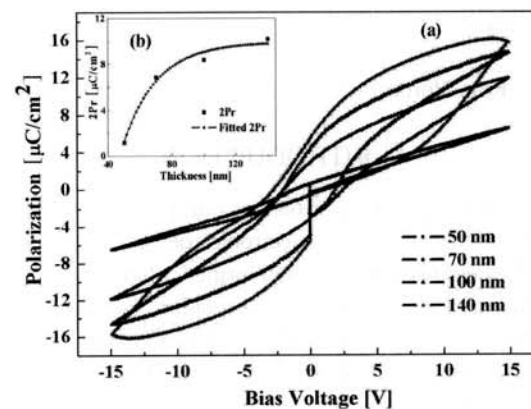


Fig. 2. (a) The polarization-voltage (P - V) hysteric curves of the PVDF-TrFE (51/49) biased at ± 15 V. (b) the variation of the $2Pr$ value according to the change of the film thickness.

The P - V hysteresis curves for PVDF-TrFE (51/49) films according to the film thickness are shown Fig. 2(a). Most studies for the thickness dependency of ferroelectric behavior of PVDF and its copolymer have shown that the remanent polarization decreased as the film thickness

became thinner[8]. Moreover, large drops of the polarization values were observed when the film thickness is below 100 nm[9]. Our results also had a similar relationship between electrical properties and the film thickness. As summarized in Fig. 2(b), the $2Pr$, the difference of the remanent polarization at 0 V, decreased gradually from 10.19 to 5.7 $\mu\text{C}/\text{cm}^2$ as the film thickness decrease from 140 to 70 nm. However, the rapid drop of $2Pr$ was observed when the thickness became more thinner, i.e 50 nm so the minimum critical thickness might be at least 70 nm for device.

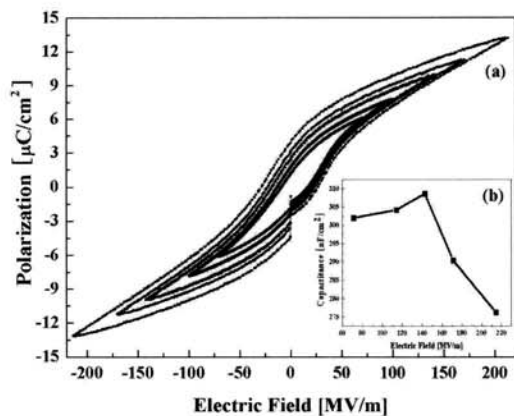


Fig. 3. (a) The polarication-electric field (P - E) curves for various bias voltages. (b) The change of capacitance according to the bias voltage.

Figure 3(a) shows the P - E curves for the PVDF-TrFE (51/49) with different electric field. The $2Pr$ was 5.7 $\mu\text{C}/\text{cm}^2$ for a bias voltage of 140 MV/m. These values are a little small as compared with results from others[10]. It might be also be caused by the coexistence of paraelectric and ferroelectric phase.

The polarization value be obtained by Precision LC parameter analyzer followed the equation that $P = C \cdot V / A$ where C is capacitance, A is the area of the capacitor and V is bias voltage. From Fig. 3(b), the capacitance increased until 140 MV/m. However, when the bias voltage over 140 MV/m was applied to the

structure, the capacitance decreased which might be attributed to the charge injection.

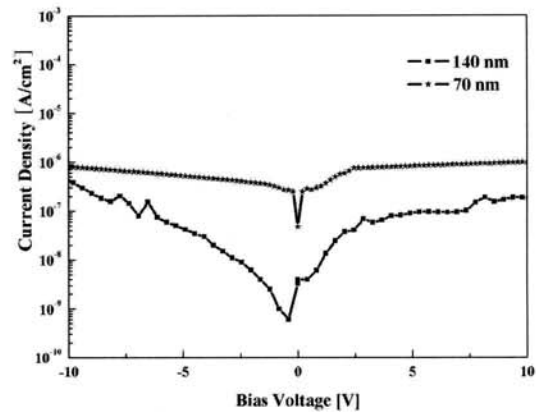


Fig. 4. The characteristic of current density-voltage (J - V) with 70 nm, 140 nm - thick film. The thicker film indicated lower current density than the thinner one and the current density of both film is under 10^{-6} at 10 V.

PVDF-TrFE copolymer plays a dielectric layer in electronic devices and thus its insulating property is one of the important properties have to be evaluated. Figure 4 shows the leakage current characteristic curves for PVDF-TrFE (51/49) films. The leakage current densities of film with 70 and 140 nm was as low as 1×10^{-6} and 4×10^{-7} A/cm^2 at 10 V, respectively. The thicker film showed slightly better insulating property for low-voltage range. Incorporation of TrFE in to VDF to form copolymer, has been known as to obtain the ferroelectric phase, but it was also known as that the leakage current along dipole moment directions in a molecule enlarge as the content of TrFE increased[11]. Sumiko Fujisaki *et al.* presented that the leakage current density of PVDF-TrFE (77/23) was 10^{-5} A/cm^2 below only 5 V[11]. In our work, however, although the $2Pr$ value was rather lower than the result of Sumiko Fujisaki *et al.* report, the leakage current density was as low as 10^{-6} A/cm^2 at 10 V even though the PVDF-TrFE (51/49) film in our work contained

larger TrFE. When we deposited the film, the treatment time was just 10 minutes for annealing. This phenomenon might be attributed to the short annealing time in our study. It is important that the leakage current could be controlled by duration of annealing time. We did not yet study the relationship between degree of crystallization and leakage current. However, from this result, we could expect that the leakage current is inverse proportion to the degree of crystallization.

4. CONCLUSION

In this work, we investigated the crystalline phase and electrical properties of the PVDF-TrFE (51/49) thin film with different thickness. From XRD sheets, the thicker film showed better crystallization. It was revealed from the P - V characteristics of the Au/PVDF-TrFE (51/49)/Pt/Ti/SiO₂/Si structure with different thickness of ferroelectric layer that the remanent polarization value decreased, as the film thickness decreased and thickness of the films could be selected from 50 to 140 nm for thin film FeRAM. The thicker film showed lower leakage current density than the thinner one as leakage current density of the 70 nm- and 140 nm-thick films were 1×10^{-6} and 4×10^{-7} A/cm² at 10 V, respectively. We can expect from these results that the electrical properties of the devices particularly ferroelectric thin film transistor using PVDF-TrFE copolymer were able to be on the trade-off relationship between the remanent polarization with the bias voltage and the leakage current.

REFERENCES

- [1] N. Koch, "Organic electronic devices and their functional interfaces", *Chemphyschem*, Vol. 8, p. 1438, 2007.
- [2] S.-H. Park, J.-T. Kim, and D.-C. Lee, "The effect of ion contribution to the dielectric properties of β -PVDF thin film fabricated by vapor deposition method", *J. of KIEEME (in Korean)*, Vol. 11, No. 11, p. 1007, 1998.
- [3] R. C. G. Naber, C. Tanase, P. W. M. Blom, G. H. Gelinck, A. W. Marsman, F. J. Touwslager, S. Setayesh, and D. M. D. Leeuw, "High-performance solution-processed polymer ferroelectric field-effect transistors", *Nature Materials*, Vol. 4, p. 243, 2005.
- [4] J. H. Kim, D. W. Kim, H. S. Jeon, and B. E. Park, "Electrical characteristic of metal-ferroelectric-semiconductor structures based on poly(Vinylidene fluoride)", *Jpn. J. of Appl. Phys.*, Vol. 46, p. 6976, 2007.
- [5] R. C. G. Naber, B. de Boer, P. W. M. Blom, and D. M. de Leeuw, "Low-voltage polymer field-effect transistors for nonvolatile memories", *Appl. Phys. Lett.*, Vol. 87, p. 203509, 2005.
- [6] A. C. Nguyen and P. S. Lee, "Ferroelectric copolymer P(VDF-TrFE) as gate dielectric in organic field effect transistors for memory application devices", *Emerging Technologies-Nanoelectronics, IEEE conference on*, p. 179, 2006.
- [7] H. Su, A. Strachan, and W. A. Goddard, "Density functional theory and molecular dynamics studies of the energetics and kinetics of electroactive polymers : PVDF and P(VDF-TrFE)", *Phys. Rev. B*, Vol. 70, p. 064101, 2004.
- [8] K. Kimura and H. Ohigashi, "Polarization behavior in vinylidene fluoride-trifluoroethylene copolymer thin films", *Jpn. J. Appl. Phys.*, Vol. 25, p. 383, 1986.
- [9] N. Tsutsumi, A. Ueyasu, W. Sakai, and C. K. Chiang, "Crystalline structures and ferroelectric properties of ultrathin films of vinylidene fluoride and trifluoroethylene copolymer", *Thin Solid Films*, Vol. 340, p. 340, 2005.
- [10] Y. Tajitsu, "Effects of thickness on ferroelectricity in vinylidene fluoride and trifluoroethylene copolymers", *Jpn. J. Appl. Phys., Part 1*, Vol. 34, p. 5418, 1995.
- [11] S. Fujisaki, Y. Fujisaki, and H. Ishiwara, "Low-voltage operation of ferroelectric poly(vinylidene fluoride-trifluoroethylene) copolymer capacitors and metal-ferroelectric-insulator-semiconductor diodes", *Appl. Phys. Lett.*, Vol. 90, p. 162902, 2007.