

## Electrical Properties of Metal-Ferroelectric-Semiconductor Structures Based on Ferroelectric P(VDF-TrFE) Copolymer Film

Gwang-Geun Lee, Hyeong-Jin Park, Hui-Seong Han, Byung-Eun Park  
University of Seoul

**Abstract :** A poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) copolymer thin film having  $\beta$  phase was prepared by sol-gel method. The electrical properties of the film were studied to evaluate the possibility for applying to a ferroelectric random access memory. In order to characterize its electrical properties, we produced a MFS (metal-ferroelectric-semiconductor) structure by evaporation of Au electrodes. The C-V (capacitance-voltage) measurement revealed that the Au/P(VDF-TrFE)/Si structure with a 4 wt% film had a memory window width of about 0.5V for a bias voltage sweep of 1V.

**Key Words :** P(VDF-TrFE), MFS, Memory window width

### 1. Introduction

Recently, many studies on ferroelectric-gate field-effect transistors (FeFETs) for nonvolatile memory device have become more. But the direct deposition on a Si substrate causes the inter-diffusion. For that reasons, MFIS structure with a buffer layer such as  $\text{HfO}_2$ ,  $\text{Y}_2\text{O}_3$  and  $\text{ZrO}_2$  was applied to FeFETs [1,2]. On the other hand, because P(VDF-TrFE) was deposited at a low temperature, such a inter-diffusion do not matter. Since H. Kawai discovered the piezoelectricity in poly (vinylidene fluoride) (P(VDF)), Bergman and Wada found the pyroelectricity in P(VDF) and its copolymer poly (vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)). Their ferroelectricity, piezoelectricity and pyroelectricity have been intensively studied for application in no-volatile memory in organic electronic devices [3,4].

It has been reported that the copolymer could be directly crystallized into  $\beta$ -phase when it suffered heat-treatment at temperature between the curie transition temperature ( $T_c$ ) and melting temperature ( $T_m$ ). As well, the copolymer must contain VDF molar content more than 50 mol%. And P(VDF-TrFE) copolymer with VDF of 70~80 mol% exhibits the higher polar than the others [5,6]. In the copolymer of VDF and TrFE, the molar content ratio of VDF controls the spontaneous polarization value. On the other hand, crystal structure and crystallinity are decided upon the content ratio of TrFE [7]. For that reasons, we have employed a copolymer of VDF and TrFE with 75/25 molar ratio.

### 2. Experiment

The P(VDF-TrFE) copolymer powder with VDF 75% and TrFE 25% was dissolved in a DMF (dimethylformide) solvent at 60°C on a hot-plate for 24 hours. P-type Si(100) wafer were used as substrates. After cleaning by using a

standard process ( acetone, methanol and de-ionized water) and the substrate was dipped in a BOE (buffer oxide etchant) to remove naturally grown  $\text{SiO}_2$ . P(VDF-TrFE) films were prepared by using a spin-coating method. The sol-gel solutions were deposited on cleaned Si(100) substrates by using a spin-coating method from 500rpm to 2500rpm. The deposited layer was dried at 165°C for 30 min in air on a hot-plate to remove the residual solvents and to improve crystallinity. The thickness of the deposited films were about 100nm, respectively. Then, Au films as circular upper electrodes were fabricated onto the P(VDF-TrFE) film surface by shadow mask (diameter = 200 $\mu\text{m}$  ). The ohmic contact was formed to the back side of the silicon with a vacuum-evaporated gold film. The C-V characteristics were measured by using a HP 4280A C-V plotter. And the J-V characteristic was measured by using a Agilent 4155C.

### 3. Results and Discussion

Figure 1 show the C-V characteristics of the P(VDF-TrFE)/Si structure measured at very low voltage 1 MHz. The C-V curves were measured at a bias sweep rang from  $\pm 0.1\text{V}$  to  $\pm 1\text{V}$ . The C-V plot showed a hysteresis loop, with a clockwise trace as indicated by the arrows in Figure 1. This loop indicated the ferroelectric behavior of the P(VDF-TrFE) film. Figure 1 shows the hysteresis loop was not yet saturated for a bias sweep voltage of  $\pm 1\text{V}$  whereas for a bias sweep voltage above  $\pm 1\text{V}$ , it was setting into saturation. Figure 2 show the saturated hysteresis loop. It was encouraging result that the hysteresis loop was saturated and the memory window width was about 0.5V at a sweep voltage of  $\pm 1\text{V}$ . However, using this film in low-voltage memory devices operating at 1V improved the leakage current problem.

Figure 3 show the J-V characteristics of the P(VDF-TrFE)/Si structure. The leakage current densities of P(VDF-TrFE) film was  $2.8 \times 10^{-4} \text{A/cm}^2$ , respectively, at 5V.

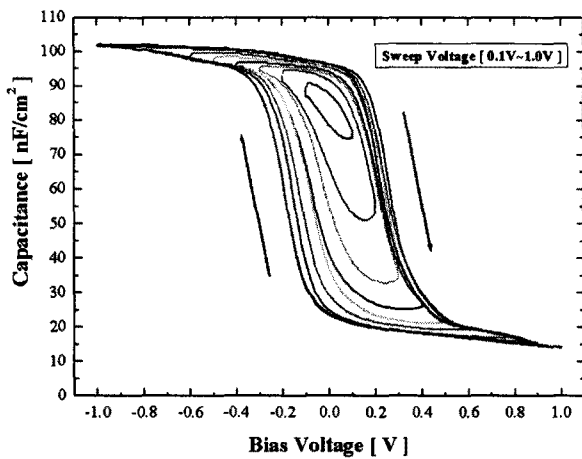


Figure 1. C-V characteristics for Au/P(VDF-TrFE)/Si structure (the voltage was swept from  $\pm 0.1V$  to  $\pm 1V$ ).

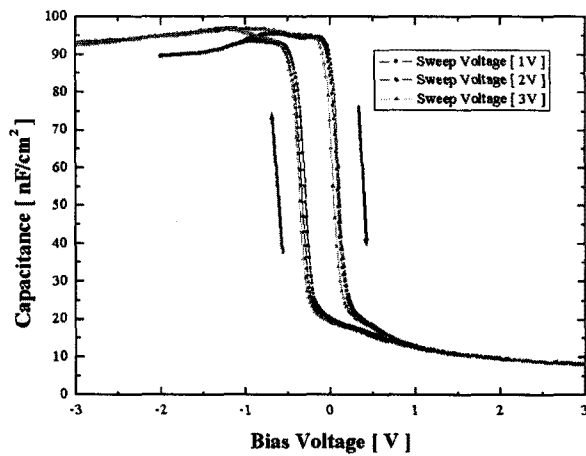


Figure 2. C-V characteristics for Au/P(VDF-TrFE)/Si structure (the voltage was swept from  $\pm 1V$  to  $\pm 3V$ ).

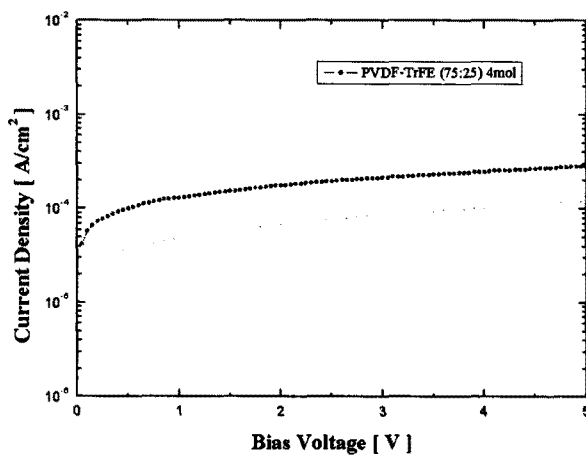


Figure 3. J-V characteristics for Au/P(VDF-TrFE)/Si structure

#### 4. Conclusion

We formed P(VDF-TrFE) thin films on Si(100) substrates by using a sol-gel method. In the Au/P(VDF-TrFE)/Si structures, the hysteresis loops result from the ferroelectricity

of P(VDF-TrFE) with a  $\beta$  phase were observed in the C-V characteristics. The memory window width was about 0.5V for the sweep range of 1V. To improve the leakage current and crystallinity, we conclude from these results that a copolymer of P(VDF-TrFE) is one of the most promising candidates for a ferroelectric organic copolymer.

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