Ferroelectric P(VDF/TrFE) Copolymers in Low-Cost Non-Volatile Data Storage Applications

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Introduction

Non-volatile random access memory (NV-RAM) devices based on ferroelectric polymers have the potential to overcome many of the fabrication issues faced in the inorganic semiconductor industry. A recent review on polymer-based devices by Forrest [1] highlights the importance of this rapidly growing field. More recently, LG, Korea has demonstrated a low power SPM probe-based high density data storage system which uses a new read-write mechanism called "Thermo-piezoelectric method" in which the cantilever tip equipped with a heater is used for making an indentation (stands for a logical '1') on a PMMA film [2]. However, the main drawback is that, writing data by this thermal method changes the polymer surface morphology and limits its usage to Write-Once-Read-Many (WORM) applications.

Replacing PMMA with ferroelectric poly(vinylidene fluoride-trifluoroethylene)(P(VDF/TrFE)) copolymer ultrathin films is of even greater interest in the fabrication of NV-RAM for Write-Many-Read-Many (WMRM) applications. Their memory function with "non-destructive" readout capability is performed by electrically switching their dipoles between the '1' and '0' states in NV-RAM device with much larger remnant polarization ($\pm P_r$), which is mainly dependent on the degree of crystallinity, which in turn is dependent on film thickness and uniform film surface [3].

In this paper, we report the fabrication of Metal-Ferroelectric polymer-Metal (MFM) single bit device based on P(VDF/TrFE(72/28) ultrathin films with uniform film surface, faster dipole switching time and longer data retention time. Our main objective is to study the ferroelectric response of P(VDF/TrFE(72/28) ultrathin films under external electric field using polarization (P-E) studies and to study their piezoelectric response and domain structure using EFM technique.

Experimental

VDF-TrFE(72/28) copolymer samples (herein mentioned as VDF 72% copolymer) in the form of pellets have been obtained from Solvay, USA. 100 and 250 nm ultrathin films were prepared by spin casting different wt% of VDF 72% copolymer in MEK solvent with a spin-coater (1500 rpm/30 s) under N_2 atmosphere over ITO glass. AFM images were obtained using XE-100 (PSIA, Korea) equipped with a heating stage. FTIR-GIRAS data were collected using Bruker-IFS66V spectrometer with 300 scans at an incidence angle of ca. 85° from the normal to the surface. For electrical studies, aluminum electrodes were vacuum-deposited on the top surface of the cast films. P-E hysteresis curve was measured on a ferroelectric tester (Precision LC, Radiant Technologies, USA).

Results and discussion

AFM studies. As-cast (AC) and annealed (AN, 120°C, 3h) samples exhibited smaller crystalline size and relatively uniform film thickness as evidenced from their respective histograms (*Figure not shown here*). Melt (200°C, 10 min)-quenched (MQ) and melt (200°C, 10 min)-slowly cooled (MSC)(-2°C/min) samples exhibited drastically changed surface morphology with non-uniform film thickness.

GIRAS Studies. From GIRAS data (*Figure not shown here*), after spin-casting, most polymer chains were preferentially oriented along the substrate surface but still some chains exists in a random state, which after annealing, undergoes thermal relaxation resulting in preferential orientation of trans-zigzag chains parallel to the substrate surface with the dipoles parallel along the poling direction [4]. Correlating GIRAS with AFM data, AC and AN method was found to be best suitable method for preparing samples with maximum dipole orientation along the poling direction.

P-E studies. VDF 72% copolymer 100 nm-thick AN film, when subjected to varying external electric field under bias voltage at 30°C, exhibit dielectric-to-ferroelectric behavior at and above 11 V (*Figure not shown here*). For the above sample, drastic changes in both coercive field (E_c) and P_r values were observed during heating and cooling near the T_c range due to the phase transition between ferro (polar) ↔ paraelectric (non-polar) phase. From polarization studies, it is suggested that the data written in either '1' ($+P_r$) or '0' ($-P_r$) state can be read by applying bias DC or AC voltage below $\pm E_c$.

DC-EFM Studies. Figures 1 (a) and (b) shows the EFM amplitude and phase images observed during data write '1' state and erase '0' state, respectively (Tip and sample bias voltage: 10V). The effect of varying tip bias is also shown in Figures 1(c) and (d). Using EFM data, the change in dipole moment vectors along the applied field direction and the resultant change in amplitude or phase image for '1 or 0' state were monitored without causing any change in the surface morphology and hence have much wider and better WMRM storage applications than that mentioned in Ref. [2].

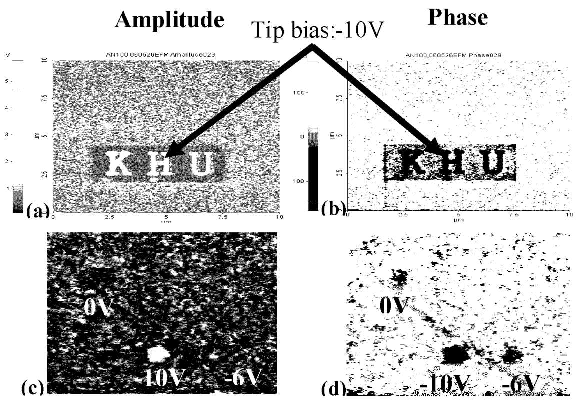

Figure 1. EFM amplitude and phase images of VDF 72% copolymer 100 nm (AN) film during (a) data write state and (b) data erase state, (c) Effect of varying tip bias (Tip: NSC36 Ti/Pt coated tip, holding time: 500ms) during write state and (d) during erase state respectively.

Conclusions

For P(VDF/TrFE)(72/28) copolymer samples, AFM and FTIR-GIRAS were complementary in analyzing surface crystalline morphology and the resultant change in chain orientation with varying thermal history. DC-EFM technique was used to 'write-read-erase' the data on the memory bit in a much faster time than P-E studies. However, from conventional MFIS device, it is difficult to read if the already written data is either '1 or 0'. Hence, in our future studies, we propose a novel set-up resembling MFMIMFM device using which we can use simple electrical studies like capacitance (C-E) measurements to non-destructively 'read' if the data written is either '1 or 0'. The results obtained from this study will enable us to have a good understanding of the ferroelectric and piezoelectric behavior of P(VDF/TrFE)(72/28) thin films suitable for futuristic high density data storage applications.

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