



Chemical bonding states at the polymer/metal interface and their effects on the capacitance–voltage characteristics of the ferroelectric poly(vinylidene fluoride-trifluoroethylene) copolymer thin films



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ABSTRACT

The electrical and ferroelectric properties with different amounts of chemical bonding states at the polymer/metal interface were examined quantitatively in a ferroelectric copolymer poly(vinylidene fluoride-trifluoroethylene) film sandwiched between the top and bottom electrodes on which the surface had been modified by rapid thermal processing in a N₂ atmosphere. The capacitors with the heat-treated bottom electrodes at different temperatures showed a lower charge storing capacitance. Ultraviolet photoelectron spectroscopy showed that the capacitance enhancement and field shift to lower coercive value resulted from the relatively larger increase in anions (N,O) than cations (Ti) and the reduction of N–C bonding in the reaction product (TiN_xO_y) on the surface of the bottom electrode, respectively.

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1. Introduction

Organic ferroelectric polymers have attracted considerable interest for their use as functional devices, such as flexible display devices, energy transduction, and information storage and sensors [1–3]. Much of this interest stems from the belief that ferroelectric polymers might provide cheaper and easier processing alternatives to inorganic perovskite ceramics currently employed in ferroelectric random access memory [4–6], or suppress the formation of the interfacial layers between ferroelectric films and the Si substrate [7]. Many studies have examined the ferroelectric properties and functional performance of ferroelectric polymer thin films [8–13]. More recently, the surface and interface between thin polymer films and metal have attracted attention because they play significant roles in the functional performance of thin films. In the metal/ferroelectric film/metal (MFM) structure of capacitors, a polymer/metal interface with a higher work function has significant effects on the coercive field (E_c), polarization switching and leakage current of ferroelectric poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] copolymer thin films [14–16]. In addition to studies of the ferroelectric polymer/metal interface, the introduction of suitable interlayers between the metal electrode and ferroelectric material [P(VDF-TrFE)] has attracted attention as a solution to the problems of a large E_c , degradation of the polarization level, and long ferroelectric switching time when the thickness

of the ferroelectric polymer is reduced to less than 100 nm [17–19]. These interlayers include the polymeric proton conductor, such as poly(styrene sulfonic) acid and poly(vinyl phosphonic) acid, and conducting polymer or oligomer, such as doped polypyrrole, polyaniline, polythiophene, and poly(3,4-ethylenedioxythiophene).

Despite the extensive research on the synthesis, frequency dependent fatigue, chemical stability, thermal history and ferroelectric polymer/metal interface, there have been few fundamental studies on the ferroelectric properties of organic [P(VDF-TrFE)] copolymer films with the different chemical bonding states at the polymer/metal interface and on the metal electrode surface. The aims of this study were to examine the possibility of controlling the electrode surface and hence the ferroelectric polymer/electrode interface to reduce the E_c of organic [P(VDF-TrFE)] copolymer films, which is essential for fabricating a device with low voltage switching. The surface layer of the metal electrode TiN was modified to TiN_xO_y and used as an interlayer between the ferroelectric polymer and metal electrode instead of using a polymeric conductive electrode on a bottom electrode in MFM capacitors.

2. Experiments

25 nm TiN films were deposited on an 8" (100)-oriented Si-substrate as a bottom electrode by reactive magnetron sputtering (AMAT, ENDURA 5500) from a Ti target in a N₂ ambient at 300 °C. Two of these wafers were then annealed by rapid thermal annealing (RTA, Metron AG Heatpulse 8800) of the TiN films in a N₂ ambient for 30 s at different

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temperatures (600 and 750 °C) to modify the chemical states of the TiN surface. The surface chemistry and chemical composition of the films were examined by X-ray photoelectron spectroscopy (XPS, PHI 5000 Versaprobe, ULVAC-PHI) with a take-off angle of 90° in a base pressure of 1×10^{-9} Torr. The energy analyzer of the XPS system is a concentric hemispherical analyzer (CHA). The base pressure in the analysis chamber was maintained lower than 1×10^{-9} Torr and a monochromatic Al K α (1486.6 eV) X-ray source was used (25 W) filament current (16.7 mA). The parameters for survey scans were: pass energy 117.4 eV; dwell time 50 ms; and energy step 0.5 eV in constant analyzer energy (CAE) mode. Sputtering ion beam species Ne, at an acceleration voltage of 2 kV and with 5.0 mPa external base pressure of Ne gas container (external working pressure is 1.0 mPa). High resolution XP spectra were obtained at a pass energy of 23.5 eV, an energy step of 0.025 eV, and other parameters the same as for survey scans. High resolution XPS data were deconvoluted using Fitt (version 1.2) software developed by ESCA Lab. in Seoul National University, Korea. All the spectra have been shifted with respect to binding energy of surface carbon (248.5 eV) and compared. In the peak fit analysis, Shirley type background and Lorentzian curves convoluted with a Gaussian profile were employed. Lorentzian width was fixed at 0.4 eV and Doniac–Sunsic factor for asymmetry of peak shape was not employed. Other parameters were selectively fixed or unfixed and vice versa to determine fit parameters of exhibiting the least fit errors. In order to allow a highly controlled and reproducible deposition of thin film on the desired substrate [20] and to scale down the chip size, therefore to increase integrated-circuit density in the micro-electronic fabrication, a 370 nm single layer [P(VDF-TrFE)] copolymer thin film was deposited by spin-coating at 3000 rpm for 30 s on the TiN_xO_y from the solution prepared by dissolving 0.35 g of the [P(52% VDF-48% TrFE)] copolymer powder (99.9%, SOLVAY) in 5 mL of diethyl carbonate (99.9%, Aldrich) followed by stirring for 24 h at 60 °C. The films were annealed at 140 °C for 1 h in ambient air to enhance or to maximize a crystalline phase of the [P(VDF-TrFE)] copolymer, which induces the maximum remnant polarization in the characteristics of electric displacement and the electric field [21]. Through a metal shadow mask, the Au top electrodes were deposited on the ferroelectric films by electron-beam evaporation which provides

the metal electrode or MFM capacitor with an easy and simple process to be optimized without the presence of a dead layer between the metal electrode and ferroelectric polymer. In particular, TiN is used as diffusion barriers in Al/TiN/Ti structures and shows excellent stability during a subsequent annealing at 600 °C. Therefore, ferroelectric properties of thin MFM capacitor can be improved by suppressing carbon diffusion to substrate during an annealing at 140 °C. The X-ray diffraction (XRD) was used to assess the phases and crystallographic textures of the product films. Routine analysis was performed using a 2 θ diffractometer (X'Pert-PRO MRD, PANalytical) with monochromatized Cu-K radiation that was supplied by a rotating anode generator operating at 40 kV and 300 mA with a scanning speed of 2°/min and a step of 0.01°. Scanning electron microscopy (SEM) of the film surfaces was obtained with a field-emission SEM (S-4800, Hitachi) operating at 10 keV. The capacitance versus voltage (C–V) characteristics were measured by sweeping the voltage at room temperature.

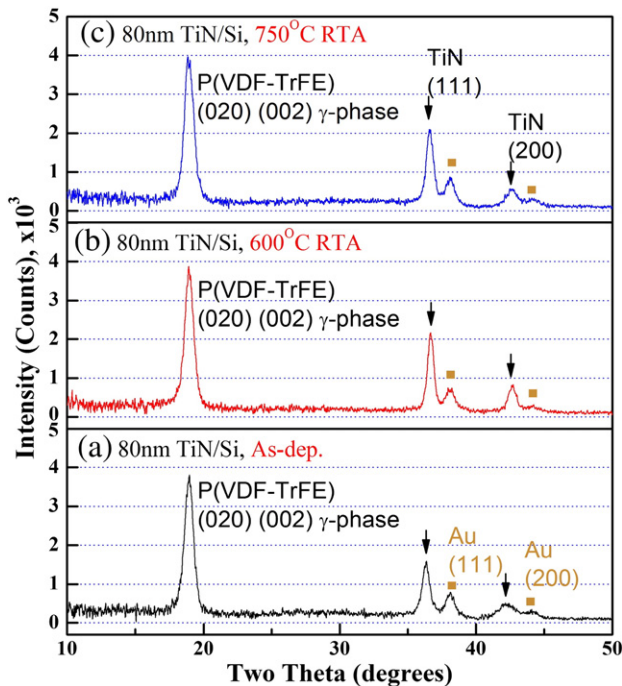


Fig. 1. XRD patterns from the Au/P(52% VDF-48% TrFE)/TiN capacitors with TiN bottom electrodes: (a) as-deposited at 300 °C in a N₂ ambient, (b) RTA treated at 600 °C for 30 s in a N₂ ambient, and (c) RTA treated at 750 °C for 30 s in a N₂ ambient.

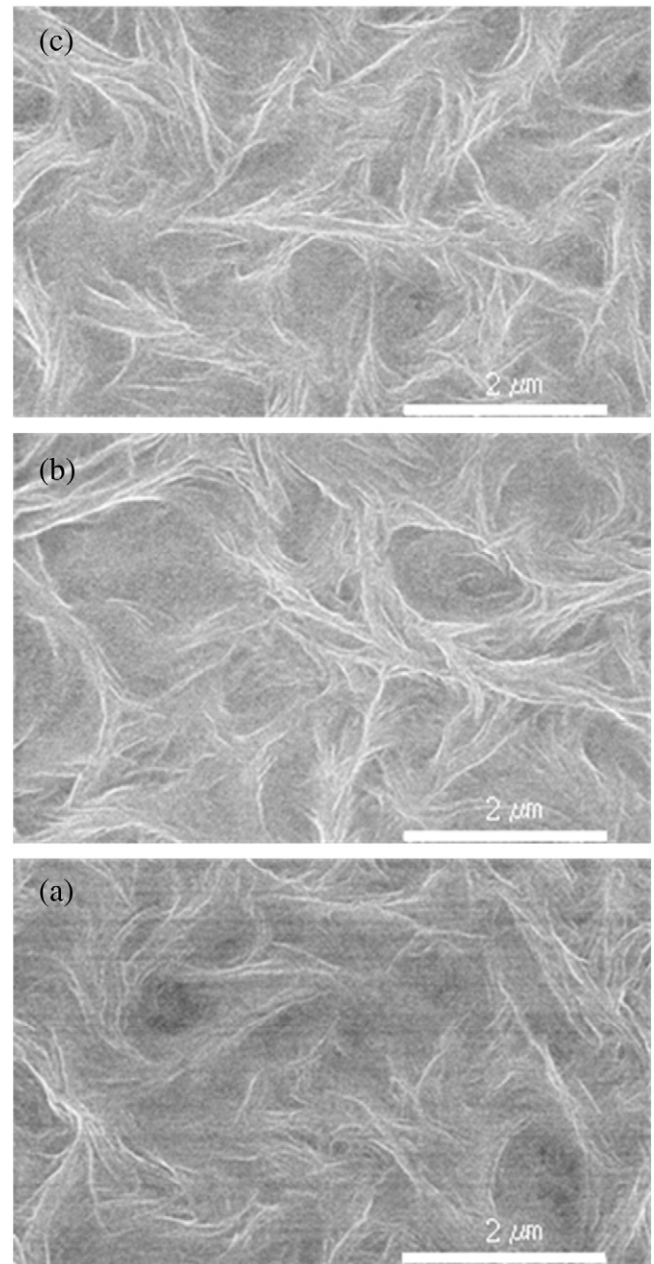


Fig. 2. SEM micrographs of the P(52% VDF-48% TrFE) thin films on TiN bottom electrode: (a) as-deposited at 300 °C in a N₂ ambient, (b) RTA treated at 600 °C for 30 s in a N₂ ambient, and (c) RTA treated at 750 °C for 30 s in a N₂ ambient.

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