Effect of electric-field-assisted thermal annealing of poly(4-vinylphenol) film on its dielectric constant

Ji Hoon Park and Eugene Kim[a)]

Department of Information Display, Hongik University, Seoul 121-791 Republic of Korea

We investigated the effect of annealing a polymeric dielectric film in the presence of an oscillating electric field on its dielectric constant. Films were prepared with the vertical structure of electrode/poly(4-vinylphenol)/electrode and annealed at a temperature above the glass transition temperature while applying an ac electric field ranging from 0 to 6 V at various frequencies in the hope of altering the arrangement of polymer chains through conformational transitions influenced by the orientational polarization of the polar phenol groups. It was found that the dielectric constant increased significantly by about 30% when the annealing frequency corresponded to that at which dielectric relaxation takes place effectively. © *2008 American Institute of Physics.*
[DOI: 10.1063/1.2896603]

Organic thin-film transistors (TFTs) including polymer TFTs have attracted a great deal of attention over the last decade.[1] This trend has been motivated by the merits of organic materials, such as their solution processability, suitable mechanical flexibility for realizing flexible devices, and low processing cost. Recently, a number of polymer dielectric materials such as poly(4-vinylphenol) (PVP) [dielectric constant ε is 4.0–4.6 (Refs. 2 and 3)] and poly(methylmethacrylate) [ε is 2.5–2.9 (Ref. 4)] have been employed in field effect transistors and their performances have been investigated in depth.[2–6] In order to realize TFTs with satisfactory characteristics, the polymer dielectric film should meet the following requirements:[7] high capacitance, low leakage current, and smooth surface. PVP is possibly the polymer dielectric with the highest field effect mobility[2] and it was reported that a small increase in the dielectric constant resulted in a dramatic increase in mobility.[4] Many attempts have been made to improve the performance of polymer gate dielectrics including mixing the polymer with TiO_2 nanoparticles[8] and fabricating polymer-oxide bilayers.[9] Ultrathin gate dielectrics made of self-assembled monolayers[10] and thin polymers[11] have also been tried with the intention of increasing the capacitance of the gate dielectric.

The molecular arrangement of polymeric materials may be changed when they are under the influence of mechanical shear[12] or an electric field.[13,14] Processes utilizing such external forces can increase the net dipole moment of the molecules, which is expected to raise the dielectric constant. In the present work, we applied an external ac electric field varying from 0 to 6 V to a PVP dielectric layer at different frequencies at a temperature (175 °C) above the glass transition temperature (T_g) of the polymer (151 °C). The polymer film has to be heated to a temperature above its T_g for the collective conformational transitions to take place under an electric field, which would result in the intentional positional rearrangement of the PVP segments made of the vinyl backbone and dangling phenol groups.

A bottom Al electrode consisting of a 3 mm wide stripe was thermally evaporated through a metal mask on corning glass, on which 12 wt % PVP solution in propylene glycol monomethyl ether acetate was spin coated. PVP was purchased from Sigma–Aldrich (Catalog No. 436223, molecular weight=20 000) and used without further purification. The thicknesses of the films were determined to be 330 nm by surface profilometry. The polymer film was precured in a vacuum oven at 175 °C for 1 h, in order to eliminate any residual solvent and to reduce the excess free volume induced during the spin-coating process.[15] A top Al electrode consisting of a 3 mm wide stripe was sequentially evaporated across the underlying Al electrode (the defined area of the PVP capacitor was 9 mm²). We then performed postannealing in the presence of an ac or dc electric field *in situ* in an inert N_2 gas-filled oven at 175 °C for 1 h. A function generator was utilized to generate a sine wave with an amplitude of 3 V which was superposed with a dc signal of 3 V (i.e., ranging from 0 to 6 V which was within the range of dielectric strength as explained below). In the case of the dc field experiment, a voltage of 6 V was applied. After the annealing process, the device was quenched immediately to room temperature by transferring it onto a Cu plate. The cooling process was conducted with the electric field turned on, in order not to allow the PVP chains to relax back to their equilibrium conformation. Current-voltage measurements (Agilent4155C) and ac impedance measurements (HP4192A) were conducted both at 175 °C and room temperature after the postannealing.

Figure 1 shows the current density–electric field characteristics of the Al/PVP/Al device at 175 °C (unfilled circles) and room temperature (filled circles). The dielectric strength was defined as the electric field at which the leakage current density exceeds ∼1 $\mu A/cm^2$ (Ref. 16) (horizontal dashed line in Fig. 1). An electric field of about 0.2 MV/cm was judged to be the maximum value at which dielectric breakdown could be avoided at 175 °C and the vertical dashed line in Fig. 1 indicates the electric field (0.18 MV/cm) applied to the PVP films during the electric field-assisted thermal annealing.

The impedance spectra were obtained and evaluated systematically to elucidate the effect of the molecular arrangements on the dielectric properties of the device. Figure 2 displays the capacitance of our Al/PVP/Al device postan-

a)Author to whom correspondence should be addressed. Tel.: 82-2-320-1463. FAX: 82-2-3142-0335. Electronic mail: ekim@hongik.ac.kr.
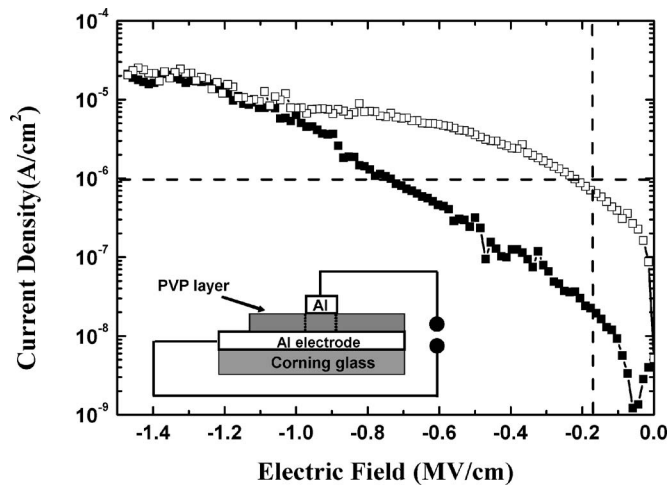
FIG. 1. Current density–electric field characteristic of Al/PVP/Al device (schematic view), characterized at 175 °C *in situ* (□) and at room temperature (■). The dielectric strength was defined as the electric field at which the leakage current density exceeds ~1 μA/cm² (the horizontal dashed line). The vertical dashed line represents the electric field applied to the PVP films during electric field-assisted thermal annealing.

FIG. 3. Imaginary part (ε'') of dielectric constant as a function of frequency measured at 175 °C *in situ*. The measured complex impedance values were transformed into complex dielectric permittivity ($\varepsilon^* = \varepsilon' - j\varepsilon''$) formalism.

nealed at 10 Hz and that of the one prepared without electric field treatment. The electric field-assisted annealing increased the capacitance by as much as 30%. The observation of unstable capacitance values below 200 Hz may be connected with the corresponding viscoelastic relaxation processes of the PVP molecules.

The dielectric response is generally described in terms of the complex permittivity, $\varepsilon^* = \varepsilon' - j\varepsilon''$, where the real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts correspond to the dielectric storage and loss factor, respectively.[17] The measured complex impedance was transformed into ε^* formalism [$\varepsilon^* = 1/(j\omega C_c Z)$, where ω, C_c, and Z are the frequency, capacitance of the empty dielectric, and complex impedance, respectively]. The dielectric relaxation behavior of polymeric systems is well understood in terms of their classical reorientation motions.[18] In general, relaxation processes in polymeric systems take place over an extraordinary broad range of time scales, which is reflected in the broadening of the loss curves in the frequency domain. Figure 3 displays the ε''

values obtained *in situ* at 175 °C as a function of frequency. The dielectric loss became larger as the frequency either increased or decreased from about 3×10 kHz, suggesting that the various in-phase motions of the PVP molecules resonate with the electric fields oscillating at the corresponding frequencies. The molecular motions at lower frequencies are accompanied by the conformational transitions of the polymer backbone, which would redistribute the locations of the polar phenol groups. We also note that the peak at around 2 MHz originates from the local rotational motion of the polar −OH radical in the phenol group (β-relaxation).

In Fig. 4, we summarized the variation of the dielectric constant measured under various conditions. The dielectric constants were calculated by taking the electrode area, capacitance, and PVP film thickness into account.[4] The value of the dielectric constant obtained from the device without electric field-assisted annealing is in good agreement with the values reported elsewhere.[3,4] The dielectric constants of the devices processed at low frequencies (10, 100, and 1 kHz) increased by as much as 30%. It is of interest to note
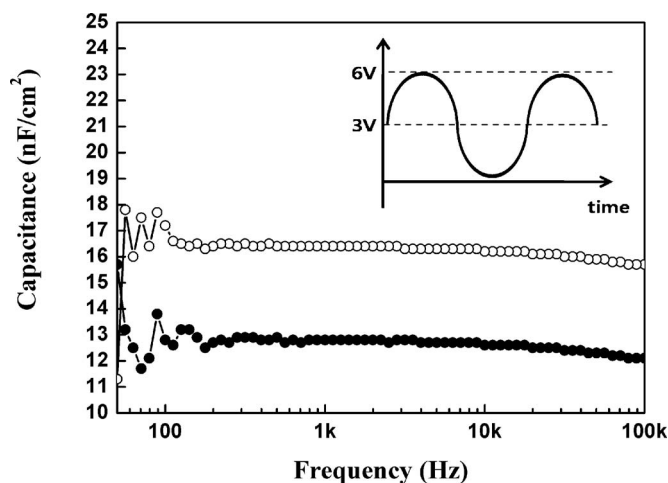

FIG. 2. Capacitance of Al/PVP/Al device as a function of frequency measured after thermal annealing (175 °C, 1 h) with (○) and without(●) treatment with an ac (10 Hz) electric field with a minimum voltage of 0 V and highest voltage of 6 V. The schematic view inside illustrates this waveform.
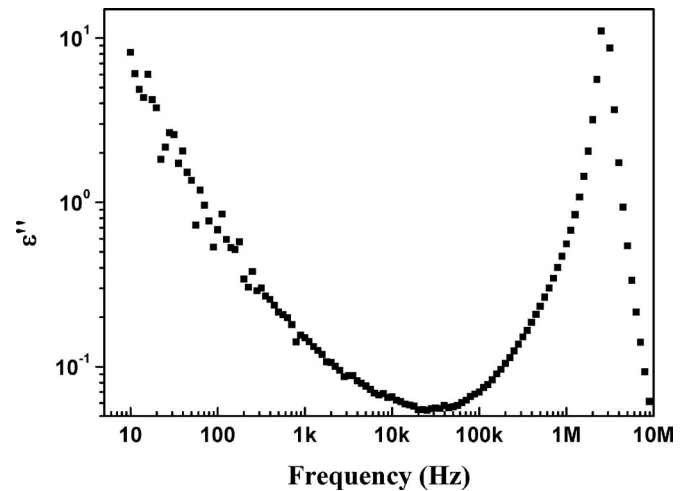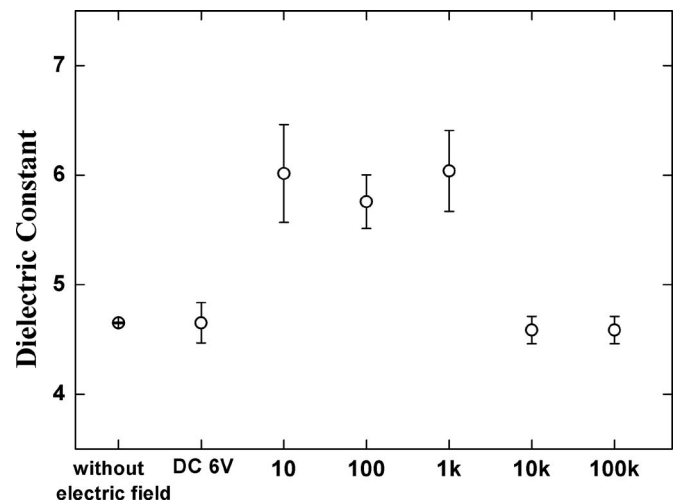

FIG. 4. Dielectric constant (ε') determined under various electric field-assisted annealing conditions: thermal annealing (175 °C, 1 h) without electric field, with dc field of 6 V, and with ac fields with a minimum voltage of 0 V and highest voltage of 6 V at various frequencies (schematic view in Fig. 2).

that the equivalent bias condition in dc form (6 V) or ac sine wave with an amplitude of 3 V did not result in any meaningful difference in the dielectric constant values. It is believed that the conformational transitions in the polar polymer molecules could be accompanied by their resonance with an oscillating electric field with a suitable frequency, resulting in the new arrangement of the chains. This leads to a structures in which local polarization by the phenol groups could be formed to a greater extent when the electric field is turned on, resulting in an increase in the net dipole moments in the vertical direction and, thus, a higher dielectric constant. At frequencies higher than 10 kHz, the conformational transition of the phenol group is judged not to keep up with the oscillations of the electric field.

In summary, we fabricated devices with the vertical structure of Al/PVP/Al to examine the effect of electric field-assisted annealing at a temperature above T_g. ac electric fields varying from 0 to 0.18 MV/cm at frequencies of 10, 100, and 1 kHz increased the capacitance by about 30% compared to the value obtained without electric field-assisted annealing. No meaningful change in the capacitance was observed when an ac bias at a frequency of 10 or 100 kHz, or a dc bias of 0.18 MV/cm was applied. The dielectric loss factor as a function of frequency was used to determine where the conformational transitions could be accompanied by their resonance with an oscillating electric field, and the result accorded well with the observation that electric field-assisted annealing was effective in such dissipative region. Our work may be able to open the way for the dielectric properties of polar organic dielectric materials to be improved by electric field-assisted annealing at a suitable frequency.

[1] C. D. Dimitrakopoulos and P. R. L. Malenfant, Adv. Mater. (Weinheim, Ger.) **14**, 99 (2002).

[2] H. Klauk, M. Halik, U. Zschieschang, G. Schmid, W. Radlik, and W. Weber, J. Appl. Phys. **92**, 5259 (2002).

[3] Y. Jang, D. H. Kim, Y. D. Park, J. H. Cho, M. Hwang, and K. Cho, Appl. Phys. Lett. **87**, 152105 (2005).

[4] J. H. Park, D. K. Hwang, J. Lee, S. Im, and E. Kim, Thin Solid Films **515**, 4041 (2007).

[5] S. Y. Park, M. Park, and H. H. Lee, Appl. Phys. Lett. **85**, 2283 (2004).

[6] Y. Jin, Z. Rang, M. I. Nathan, P. P. Ruden, C. R. Newman, and C. D. Frisbie, Appl. Phys. Lett. **85**, 4406 (2004).

[7] Z. Bao, Adv. Mater. (Weinheim, Ger.) **12**, 227 (2000).

[8] F.-C. Chen, C.-W. Chu, J. He, and Y. Yang, Appl. Phys. Lett. **85**, 3295 (2004).

[9] D. K. Hwang, C. S. Kim, J.-M. Choi, K. Lee, J. H. Park, E. Kim, H. K. Baik, J. H. Kim, and S. Im, Adv. Mater. (Weinheim, Ger.) **18**, 2299 (2006).

[10] M. Halik, H. Klauk, U. Zschieschang, G. Schmid, C. Dehm, M. Schütz, S. Maisch, F. Effenberger, M. Brunnbauer, and F. Stellacci, Nature (London) **431**, 963 (2004).

[11] L. L. Chua, P. K. H. Ho, H. Sirringhaus, and R. H. Friend, Appl. Phys. Lett. **84**, 3400 (2004).

[12] D. Maring and U. Wiesner, Macromolecules **30**, 660 (1997).

[13] T. L. Morkved, M. Lu, A. M. Urbas, E. E. Ehrichs, H. M. Jaeger, P. Mansky, and T. P. Russel, Science **273**, 931 (1996).

[14] L. Sardone, V. Palermo, E. Devaux, D. Credgington, M. Loos, G. Marletta, F. Cacialli, J. Esch, and P. Samori, Adv. Mater. (Weinheim, Ger.) **18**, 1276 (2006).

[15] D. K. Hwang, J. H. Park, J. Lee, J.-M. Choi, J. H. Choi, E. Kim, and S. Im, J. Electrochem. Soc. **153**, G203 (2006).

[16] S. Y. Yang, S. H. Kim, K. Shin, H. Jeon, and C. E. Park, Appl. Phys. Lett. **88**, 173507 (2006).

[17] E. Barsoukov and J. R. Macdonald, *Impedance Spectroscopy Theory, Experiment, and Application* (Wiley, New Jersey, 2005), pp. 7–8.

[18] R. W. Cahn, P. Haasen, and E. J. Kramer, *Materials Science and Technology: A Comprehensive Treatment*, Structure and Properties of Polymers Vol. 12 (VCH, New York, 1993), Chap. 11.