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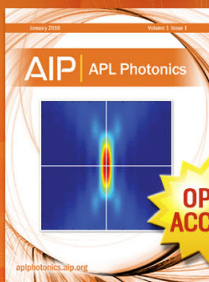
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## Spin cast ferroelectric beta poly(vinylidene fluoride) thin films via rapid thermal annealing

Seok Ju Kang, Youn Jung Park, Jinwoo Sung, Pil Sung Jo, and Cheolmin Park<sup>a)</sup>  
*Department of Materials Science and Engineering, Yonsei University, Seoul 120-749, Korea*

Kap Jin Kim

*College of Environment and Applied Chemistry, Kyung Hee University, Yongin-si, Gyeonggi-do 446-701, Korea*

Beong Ok Cho

*New Memory Process Development Team, Samsung Electronics Giheung Factory, Yongin-si, Gyeonggido 446-711, Korea*

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We describe a method of fabricating ferroelectric beta-type poly(vinylidene fluoride) (PVDF) thin films on Au substrate by the humidity controlled spin casting combined with rapid thermal treatment. Our method produces thin uniform ferroelectric PVDF film with ordered beta crystals consisting of characteristic needlelike microdomains. A capacitor with a 160 nm thick ferroelectric PVDF film exhibits the remanent polarization and coercive voltage of  $\sim 7.0 \mu\text{C}/\text{cm}^2$  and 8 V, respectively, with the temperature stability of up to 160 °C. A ferroelectric field effect transistor also shows a drain current bistability of 100 at zero gate voltage with  $\pm 20$  V gate voltage sweep. © 2008 American Institute of Physics. [DOI: 10.1063/1.2830701]

Polymer ferroelectricity originating from the bistability of permanent electrical dipoles across the long macromolecular backbone is one of the attractive properties in poly(vinylidene fluoride) (PVDF) and its copolymers with trifluoroethylene (TrFE) for the nonvolatile organic memory.<sup>1,2</sup> For an operation of the devices at low voltage, one should fabricate polymer films as thin as possible with large crystallinity and effective crystal orientation due to their relatively high coercive field of  $\sim 50$  MV/m.<sup>3</sup> Another factor for the devices based on PVDF, in particular, is how to achieve effectively the ferroelectric  $\beta$  crystals in which synchronized chain rotation of the consecutive transconfiguration, i.e., TTTT sequence provides the best polarization among other polymorphic crystalline structures of  $\alpha$  and  $\gamma$  with the configurations of TGT $\bar{G}$  and TTTG, respectively.<sup>4</sup> Furthermore, PVDF has the higher Curie temperature of  $\sim 170$  °C than that of the copolymers with TrFE which always give rise to ferroelectric  $\beta$  structure.

In spite of a number of methods to achieve the  $\beta$  crystals of several micron thick PVDF films that include mechanical stretching, electric poling, hygroscopic salts, epitaxy with KBr and rate of cooling and heating, and solvent evaporation,<sup>4-6</sup> only few works have dealt with the polymorphic transition in thin PVDF films less than 300 nm in thickness with the low operating voltage of less than 30 V. A recent work by Wang *et al.*<sup>7</sup> demonstrating ultrathin melt-drawn  $\beta$  PVDF film seems hardly useful for devices due to nonuniformity of the film. From the industrial point of view, therefore, spin coating is one of the most desirable methods for large area uniform film formation.

Our recent work has also shown PVDF thin films with polar  $\gamma$  crystals prepared by pressurizing *spin cast* thin films at certain temperature range.<sup>8</sup> It is still challenging to conve-

niently prepare uniform ferroelectric PVDF thin film with  $\beta$  crystals whose permanent polarization can switch at low voltage with high temperature stability. In this work, we present a practical way for fabricating ferroelectric thin PVDF films spin cast on Au substrate mostly with  $\beta$  crystals by the rapid thermal annealing at 150 °C following the spin coating under controlled humidity.

The crystallinity index of PVDF pellets ( $M_w = 180\,000$  g/mol, Aldrich Korea) was  $\sim 50\%$ , as reported previously.<sup>8</sup> The melting and glass transition temperatures of the polymer were 167 and  $-41$  °C, respectively. The 50–500 nm thick films were prepared by spin coating with 1%–5% solution [solvent: dimethylformamide (DMF)] on Au substrates. Rapid thermal annealing of the spin cast PVDF films was performed on the heating stage (Linkam 600) at various temperatures (the heating rate of 30 °C/min) for 2 h. Ferroelectric properties of metal/PVDF/metal capacitors with Au bottom and Al top electrodes were obtained using a virtual ground circuit (Radiant Technologies Precision LC unit), as described in the previous work.<sup>8</sup> A ferroelectric field effect transistor (FeFET) was made with Au substrate as the bottom gate on which a PVDF film was spin coated, followed by rapid thermal annealing at 150 °C. A 50 nm thick layer of poly(4-vinylphenol) (PVP) was spin coated on the PVDF film and, subsequently, a 60 nm thick pentacene was thermally evaporated (pressure of  $10^{-6}$  mB and a rate of 0.1–0.2 Å/s). Au source and drain electrodes were deposited by thermal evaporation. The transistor was characterized using Agilent technologies E5270B parameter analyzer in a dark chamber. The grazing-incidence x-ray diffraction (GIXD) was performed on the 4C2 beam line at the Pohang Accelerator Laboratory in Korea. The microstructure of PVDF was examined with atomic force microscope (AFM) (Nanoscope IV<sup>a</sup> Digital Instruments) in tapping mode. Grazing-incident reflection absorption spectra (GIRAS) were measured using Bruker-IFS66V spectrometer.

<sup>a)</sup> Author to whom correspondence should be addressed. Tel.: +82-2-2123-2833. FAX: +82-2-312-5375. Electronic mail: cmpark@yonsei.ac.kr.

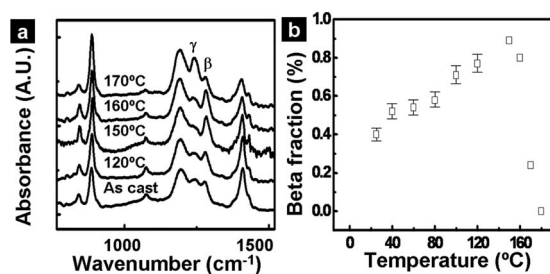


FIG. 1. (a) GIRAS spectra of thin PVDF films spin cast on Au substrate and rapidly annealed at various temperatures for 2 h. The intensity of each spectrum was rescaled for clarity. (b) The fraction of  $\beta$  crystals in the PVDF films calculated by the relative intensity of the characteristic peaks at corresponding temperature.

The typical PVDF film surface resulting from the spin casting is too rough to be applicable for capacitor in the most cases with the mixture of  $\alpha$  and  $\gamma$  crystals dependent on the solvents used. We chose DMF as a reasonable starting point for fabricating thin films with  $\beta$  crystals because polar solvents such as DMF and dimethyl sulfoxide usually give rise to thin films with dominantly  $\gamma$  crystals.<sup>9</sup> The humidity enhanced the amount of  $\beta$  crystals, consistent with the results by others,<sup>9</sup> but significantly deteriorated the film surface, inappropriate for thin film device. In order to minimize the effect of water vapor, the chamber was purged with N<sub>2</sub> gas during the film formation. The humidity was less than 20% at which a flat and smooth film exhibits dominantly  $\gamma$  crystals without the trace for  $\alpha$  crystals, as shown in Fig. 1. It should be noted that the control of humidity also makes  $\beta$  crystals formed, confirmed by the characteristic IR absorbance peaks at 840 and 1280 nm<sup>-1</sup>. The relative amount of the  $\beta$  crystals is low, approximately less than 40%, calculated by the equation  $A_{1280}/(A_{1280}+A_{1234})$  using the relative intensity of the characteristic  $\gamma$  and  $\beta$  absorptions at 1234 and 1280 cm<sup>-1</sup>, respectively.<sup>10</sup>

The portion of  $\beta$  crystals in the film was enhanced by the subsequent rapid thermal treatment. The film was subject to rapid heating with the rate of 30 °C/min up to a temperature below  $T_m$  of PVDF, leading to the directional evaporation of residual DMF along the normal of the film. A film treated with the rapid thermal annealing exhibits the portion of  $\beta$  crystals more than 90%, as shown in Fig. 1. In order to confirm the effect of the fast removal of the solvent by rapid thermal annealing on  $\beta$  crystal formation, we also treated PVDF films at different annealing temperatures from 80 to 150 °C. The portion of  $\beta$  crystals almost linearly increases with the annealing temperature up to 150 °C just below  $T_m$  of PVDF, as shown in Fig. 1(b), which indicates that the faster the removal of DMF vapor from the film, the better for formation of  $\beta$  crystals. The heat treatment above  $T_m$  of PVDF always produced either  $\gamma$  or  $\alpha$  crystals regardless of the heating rate as confirmed by both our recent work and others.<sup>8,11</sup> The melting and quenching methods, known as an effective way for  $\beta$  crystal formation in micron thick PVDF film,<sup>12</sup> dominantly generated  $\alpha$  crystals in our thin films.

In order to answer the question of whether the  $\beta$  crystals formed via rapid thermal annealing arise from the direct transition from the  $\gamma$  crystals produced during spin coating or from some seed crystals preexisting in an as-cast film, we prepared a spin coated PVDF film with almost 100%  $\gamma$  crystals by solvent annealing of saturated DMF vapor. The sub-

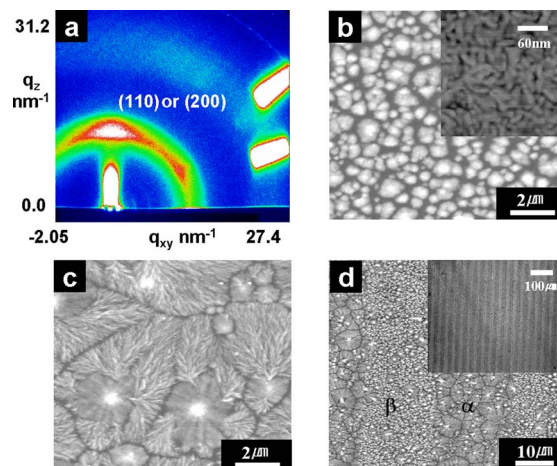


FIG. 2. (Color online) (a) 2D GIXD pattern and (b) AFM image of a 200 nm thick PVDF film spin cast and rapidly annealed at 150 °C on bare Au substrate. The inset of (b) displays a magnified image with the characteristic needlelike  $\beta$  crystals. (c) AFM images of a PVDF film spin cast and rapidly annealed on COOH-terminated SAMs treated Au substrate. AFM (d) and OM image [the inset of (d)] show micropatterned  $\beta$  and  $\alpha$  PVDF crystals.

sequent rapid thermal annealing at 150 °C for 2 h did not produce  $\beta$  crystals in the film, which indicates that the formation of  $\beta$  crystals requires some seed  $\beta$  crystals. Figure 1 also supports the argument in which ~40% of  $\beta$  crystals in an as-cast film increases with the decrease of the  $\gamma$  portion by rapid annealing.

The directional removal of residual DMF solvent in  $\beta$  PVDF thin films formed by rapid thermal annealing on Au substrates gave rise to molecular chain ordering of  $\beta$  crystals evidenced by GIXD in Fig. 2(a). The pseudo-hexagonal diffraction pattern arising from the similar lattice spacings of (110) and (200) implies that one of the two planes is preferentially aligned perpendicular to the substrate with the polymer chains preferentially oriented parallel to the Au surface. Figure 2(b) shows the microstructure of a PVDF film prepared by rapid thermal annealing where hemispherical caps are closely packed with their diameter ranging from 200 to 500 nm. The characteristic needlelike microdomains are clearly visible with the length and width of ~100 and 20 nm, respectively [the inset of Fig. 2(b)]. The structure is very similar to those with PVDF  $\beta$  crystals reported previously and distinguished with one with  $\alpha$  crystals with typical spherulites.<sup>13</sup>

In order to gain the insight of the effect of chemical nature of substrate, we employed thiol terminated self-assembled monolayers (SAMs) that can chemically link on a Au substrate. Both Au substrates treated with hydroxyl and carboxyl terminated SAMs lead to thin PVDF films with dominant  $\alpha$  crystals. The microstructure of a thin film prepared on a Au substrate with the SAMs shown in Fig. 2(c) evidences the formation of the  $\alpha$  spherulites even after rapid thermal treatment. In general, the polar substrates, on which a film is easily spin cast, always produce thin films dominantly with  $\alpha$  crystals, including Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and oxygen plasma treated Au one. It should be mentioned that a Au substrate modified with nonpolar methyl group terminated SAMs could not be used because of poor film formation.

The substrate dependent  $\beta$  crystal formation simply allows us to fabricate micropatterned  $\beta$  crystals when a PVDF thin film is spin cast and, subsequently, annealed on a chemi-

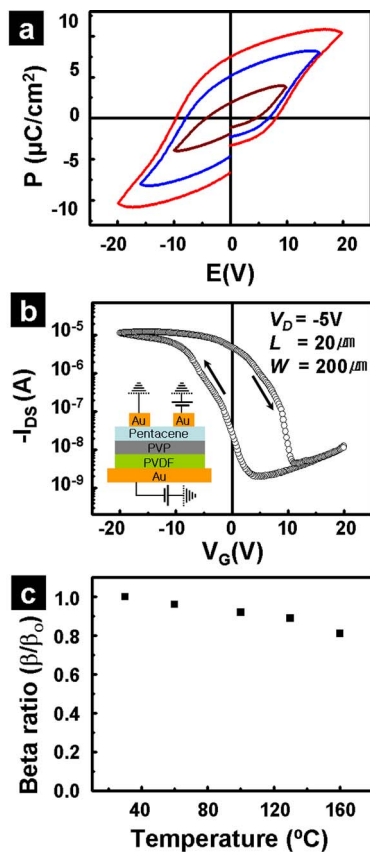


FIG. 3. (Color online) (a) Polarization  $P$  vs applied voltage  $V$  hysteresis loops of (a) 160 nm thick PVDF film rapidly annealed at 150  $^\circ\text{C}$  after spin casting. (b)  $I_D$ - $V_G$  transfer curve of pentacene OTFT with bilayered PVDF-PVP gate dielectric. The drain voltage  $V_D$ , channel length  $L$ , and width  $W$  are -5 V, 20  $\mu\text{m}$ , and 200  $\mu\text{m}$ , respectively. The arrows indicate hysteresis direction. The inset depicts the FeFET device structure. (c) The ratio of  $\beta$  crystals at various temperatures to  $\beta$  ones at room temperature measured by *in situ* GIRAS upon heating.

cally patterned Au substrate with SAMs. A 250 nm thick PVDF film prepared on a microcontact printed Au substrate with COOH-terminated SAMs apparently displays a micro-patterned image in OM, as shown in the inset of Fig. 2(d). An AFM image in Fig. 2(d) reveals the micropattern of the film consisting of one-dimensional periodic 20  $\mu\text{m}$  lines of the patterned crystals of  $\alpha$  and  $\beta$  with very sharp boundary distinguished by the characteristic spherulite and sphere cap structure, respectively.

A hysteresis loop in Fig. 3(a) was nearly saturated with the sweeping voltage of  $\pm 20$  V mainly due to the  $\beta$  crystals and their effective orientation. The electric poling exerted during voltage sweeping at low electric field was sufficient to lead to the large remanent polarization ( $P_r$ ) of 7  $\mu\text{C}/\text{cm}^2$  with the coercive voltage ( $V_c$ ) of 8 V corresponding to coercive electric field ( $E_c$ ) of  $\sim 50$  MV/m. The performance of the capacitor is comparable with that of the P(VDF-TrFE) film we observed in our previous work.<sup>14</sup> In particular, the coercive voltage is the lowest among other works reported with PVDF itself.<sup>15</sup>

We also fabricated a bottom gate pentacene FeFET with bilayered PVDF/PVP gate dielectric. The PVP layer allows not only a controlled growth of pentacene by the reduction of the substrate roughness but also low electric leakage.<sup>16</sup> The drain current ( $-I_{DS}$ ) versus gate voltage ( $V_G$ ) curve scanned with the sweep voltage of  $\pm 20$  V at a fixed  $V_{SD}$  of -5 V

shown in Fig. 3(b) clearly displays a typical ferroelectric hysteresis with the drain current bistability of  $10^2$  at zero gate bias. As expected,  $I_D$ - $V_G$  curve from the FET with paraelectric  $\alpha$ -PVDF did not show any current hysteresis at zero gate bias voltage.

One of the most important advantages of PVDF as a ferroelectric layer is its higher Curie temperature than that of its copolymers, potentially allowing the high temperature operation of polymer memory. Compared to the copolymers with Curie temperatures from 60 to 100  $^\circ\text{C}$  dependent upon the TrFE content, PVDF has the ferroelectric to paraelectric transition at its melting temperature of 167  $^\circ\text{C}$ . We measured *in situ* GIRAS of a PVDF film formed by rapid thermal annealing at 150  $^\circ\text{C}$  as a function of temperature. The ratio of the characteristic  $\beta$  absorption peak at 1280  $\text{cm}^{-1}$  obtained in a film at RT to that at the corresponding temperature is shown in Fig. 3(c). The amount of  $\beta$  crystals slightly decreases with temperature and  $\sim 80\%$  of the original  $\beta$  crystals remains up to 160  $^\circ\text{C}$ .

In conclusion, the thin PVDF films dominantly with the ordered ferroelectric  $\beta$  crystals were fabricated by rapid thermal annealing following humidity controlled spin coating on a Au substrate. The ferroelectric  $\beta$  phase of a 160 nm thick PVDF film was almost maintained up to 160  $^\circ\text{C}$  and a capacitor with the film exhibited the fairly large  $P_r$  of  $\sim 7$   $\mu\text{C}/\text{cm}^2$  with  $V_c$  of 8 V. Furthermore, the nonvolatile drain current bistability was observed in a FeFET containing PVDF gate dielectric with programming voltage of  $\pm 20$  V.

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