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Grazing Wide Angle X-ray Scattering of Ultrathin PVDF Thin Films

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Abstract
In this study, ultrathin films of PVDF-TrFE (70:30 molar ratio) with thickness of 3~20 nm were fabricated using Langmuir Blodgett (LB) technique on various substrates like Si, Au(111) and highly oriented pyrollitic graphite (HOPG). PVDF-TrFE is know to exhibit large ferroelectric character due to the presence of long chains of C-F and C-H dipoles in its all trans (TTTT) configuration. In this study the polarization orientation arising from the electric dipoles of PVDF-TrFE were investgated using grazing wide angle X-ray scattering (GIWAXS). From the GIWAXS measurement, it was found that the fabricated PVDF ultrathin films have a epitaxal crystal arrangement in the (200) direction on Au(111) and HOPG substrates. However, on Si wafers, PVDF-TrFE exhibited a random crytal orientation. The GIWAXS measurements provide insights into crystal arrangement of ferroelectric polymers like PVDF which will further help in improving the ferroelectric properties.

Keywords: GIWAXS, PVDF, ferroelectricity, Langmuir Blodgett

Background and Objective

Ferroelectric (FE) materials are those which exhibit electrically switchable spontaneous polarization due to the existence of non-centrosymmetric inversion symmetry[1]. Ultrathin FE materials are essential for the growing need for future miniaturized devices like FE random access memory. The direction of spontaneous electric polarization (up or down) in these FE thin films can be switched by the application of an external electric field leading to the formation of two electrically bi-stable states representing binary information “0” and “1”. The switched polarization is retained even after the removal of the external electric field giving rise to nonvolatility which forms the basis in memory devices. In this context, we aim to develop high-performance polymer-based ultrathin organic FE materials as an alternative to the existing inorganic materials. Currently, organic FE materials are promising alternatives for their counterparts mainly for their flexibility, ease of fabrication, and performance. In the context of organic FE, polyvinylidene fluoride or PVDF has successfully emerged as a novel alternative FE polymer material for applications in piezoelectric energy harvesting, wearable electronics, biomedical implants, wireless sensors, etc[2].

These alternative materials can also be used for future FE memories and neuromorphic computation. FE-based memristor is one such two-terminal device technology wherein FE polarization controls the resistance of the FE device thereby mimicking a human neuron[3]. For such applications, the purpose of our research is to explore the applicability of ultrathin organic FE polymers in FE memristors by fabricating FE tunnel junctions for the first time. We employ ultrathin polyvinylidene fluoride (PVDF) with 3~20 nm thickness fabricated by the Langmuir-Blodgett technique. We expect that electrons can tunnel through PVDF when sandwiched between two metals with dissimilar work functions in a tunnel junction. Tunnel junctions at the atomic scale and nanoscale can also be fabricated using a scanning probe microscope (SPM) like scanning tunneling microscopy and atomic force microscopy[4]. These methods will not only provide the topography of the samples but also give us the current-voltage characteristics of the tunnel junctions. Combining all the SPM techniques we can demonstrate the tunneling effect in PVDF atomic layers along with crucial information on the molecular arrangement and topography. In this context, material characterization of the atomically thin films is very crucial before fabricating a FE device. Since ferroelectricity is a directional quantity, properties such as crystallinity, crystal plane orientation, and molecular configuration become highly crucial for the overall FE properties. X-ray scattering experiments could provide information on the crystal structure and orientations. Combining the results from and X-ray scattering and SPM, we will demonstrate a high-performance ultrathin organic FEmemory technology in the future.

Experimental:
Grazing incidence X-ray scattering is technique to analyze the crystal structure of thin films mainly for organic and semiconductor materials which can reveal the crystal structure within 10 nm from the surface distinctly. Ultrathin Organic materials and polymers have weakly scattering crystals unlike in-organic materials with high orderliness and crystallinity, hence synchrotron radiation of high brilliance and photon flux is necessary. Refractive indices of many materials have a refractive index less than one for X-rays resulting in total reflection.

The ultrathin PVDF samples were fabricated by the Langmuir-Blodgett technique. In this method, 0.01 wt% of PVDF-TrFE in dimethylsulfoxide was dropped on the Langmuir trough containing ultrapure water. The surface pressure of the water was monitered using a Wilhemy plate. About 10 microliters of PVDF-TrFE solution was dropped using a syringe 30 times resulting in a total volume of 300 microliters. The amount of the dropping solution depends on the Langmuir trough size. After the solution was dropped, the PVDF layers were compressed by the barriers at a speed of 5 mm/s. A waiting time of 20 mins was needed after dropping the PVDF solution and compression. The PVDF layers were lifted by horizotal dipping of the substrate (Si, Au and HOPG) after the surface pressure of 5 N/m^2 was reached. To achieve multiple layers, the substrate dipping process was repeated (drying the substrate with N_2 gas between cycles) while manintaing the surface pressure. After PVDF was deposited, the samples were annealed at 140 ºC for 2 hours and cooled naturally to room temperature.

Grazing incidence angles produce a large beam footprint which increases the X-ray sample interaction. A simple experimental schematic of a typical Grazing incidence wide angle scattering (GIWAXS) as shown in Fig. 1(a), where X-rays are incident on the sample at the grazing angle (0.5° ~ 2°). A beam stopper was placed on the direct beam path to avoid damage to the detector. For collecteing the the scattered X-rays at wide angles, a 2D detector (Pilatus 300 K) was placed at 10~30 cm from the samples. Beam energies of ~12.3 keV along with a are used in the current experiment. Figure 1(b) shows schematics of ultratin PVDF crystallized epitaxially with edge-on arrangement of nano lamellae on Au (111) and HOPG substrates. Figure 1(c) shows schematics of randomly oriented PVDF nanolamellae crsystallized on Si wafer.

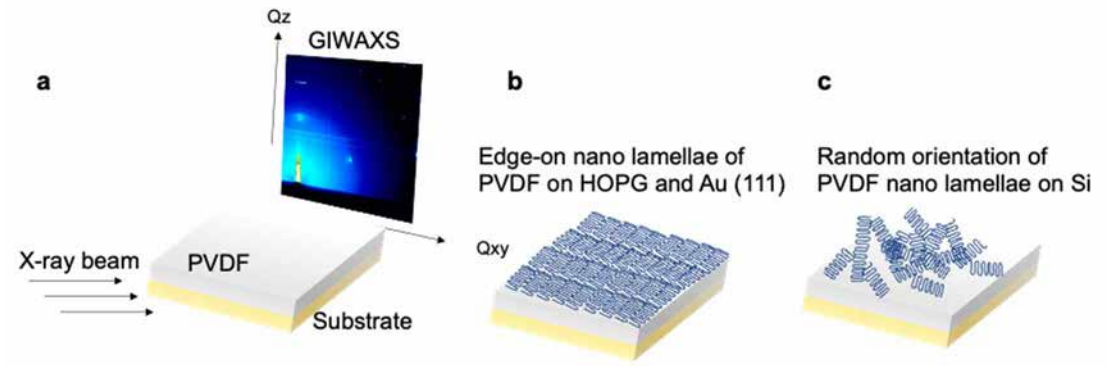

Fig. 1: (a) Schematics of the GIWAXS experiment where an X-ray beam grazes the substrate. The scattered X-rays are collected on a 2D detector placed behind the sample. (b) Schematics of 2~3 nm ultrathin PVDF nano lamellae arranged as edge-on lamellae on Au (111) substrate. (c) Schematics of 2~3 nm ultrathin PVDF lamellae arranged randomly on Si wafer.

Resuls and discussion:
Figure 2(a) shows the GIWAXS pattern of 20 nm ultrathin PVDF on Au (111) and Si substrates. In our experiment, we did not observe X-ray scattering signals from the samples with 3 nm and 10 nm thickness of PVDF. Probably, different measurements and beam with more photon flux must be implemented in the future. For the 20 nm thick samples, distinct (200) and (100) reflections are observed as bright spots for PVDF crystallized on Au (111). Similar result was observed for ultrathin PVDF crystallized on HOPG surfaces. The GIWAXS pattern thus confirm the epitxial growth of PVDF in (200) direction. This also confirmed that PVDF posess in-plane ferroelectricity in these cases. When ultrathin PVDF was crystallized on bare Si wafers, continuous reflections of PVDF (200/110) are observed. This indicated that the scattering vectors of (200/110) are randomly oriented. This also confirms that the ferroelect ric polarization direction of PVDF on Si is randomly oriented.

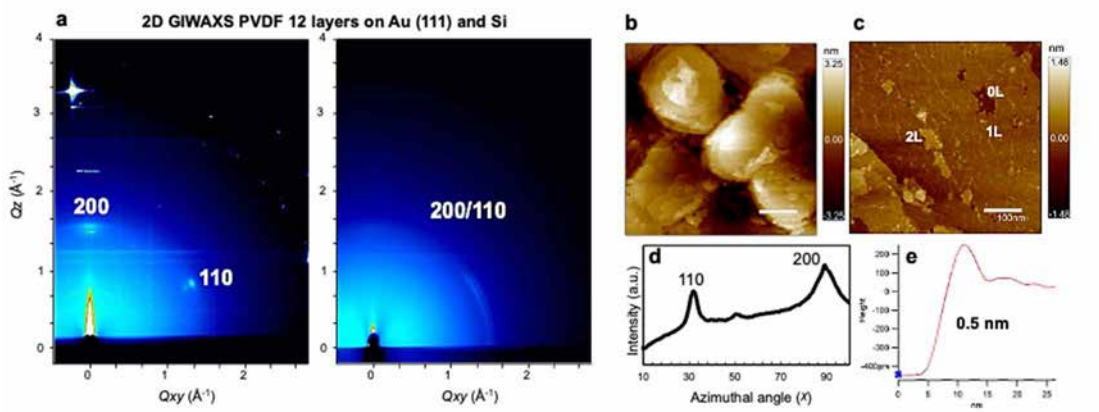

Fig. 2: (a) GIWAXS pattern of 2~3 nm ultrathin PVDF on Au (111) and Si substrates. Distinct (200) and (100) reflections are observed as bright spots for PVDF crystallized on Au (111). Continuous reflections of PVDF (200/110) are observed for the case of crystallization on a Si wafer. (b&c) AFM height images of PVDF crystallized on Au (111) surface. (d) Average azimuthal profiles of 2D GIWAXS pattern for epitaxial PVDF on Au (111). (e) AFM height profile for 1L and 0L showing layer thickness of 0.5 nm corresponding to 'b' axis of PVDF orthorhomibic crystal.

The samples were also observed from atomic force microscopy (AFM). Figure 2(b) shows the AFM height images of 2~3 nm PVDF crystallized on Au(111). From Fig. 2(c), which shows a mangnified AFM image, it is seen that PVDF crystallizes layer by layer. The number of layers are indicated on the AFM image as 0L, 1L and 2L. Figure 2(d) shows the average azimuthal profiles of 2D GIWAXS pattern for epitaxial PVDF on Au (111) which reveals the presence of highly oriented 110 and 200 planes of PVDF orthorhombic crystal as sharp peaks in the azimuthal direction. Figure 2(e) shows the cross-sectional profile of 0L to 1L showing a layer thickness of 0.5 nm corresponding to 'b' axis of PVDF orthorhomibic crystal. This also agrees with the epitaxial arrangement of PVDF on Au (111) as observed from GIWAXS. The current measurements show that the arrangement of PVDF molecules depend on the subtsrate on which it is crystallized. It is currently assumed that there is crystallographic interaction between Au (111) and HOPG on PVDF enabling an epitaxial edge-on arrangement as compared to that of Si requiring further detailed investigation.

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