

# 5 Phase Control of Molecular System Project

## – Structural investigations of molecular systems under external conditions –

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In this project, electronic correlation in molecular crystal systems is being investigated to elucidate novel phenomena such as superconductivity, ferroelectricity and charge ordering. One of our goals is to elucidate the origins of physical properties from information on the crystal structure, and so we have performed crystal structure analysis of various molecular systems including organic thin films under external conditions.

In the first period of the CMRC, we did a lot of work on the structural study of organic ferroelectrics. Recently we have succeeded in making a high-quality thin film of organic ferroelectric and evaluated it by using the diffraction of synchrotron radiation as described below.

In addition, we started the commissioning of the thin film diffractometer installed in BL-7C, Photon Factory, KEK. This will accelerate the structural investigation of thin films.

### 5-1 Few-volt operation of printed organic ferroelectric capacitor [1]

It is important to develop simple processes for fabricating ferroelectric thin films in order to meet the demand for reduced environmental load and increased production efficiency. High-performance ferroelectricity based on inorganic materials such as lead zirconate titanate and lithium niobate has been widely applied in capacitor, piezoelectric, and memory devices, although these materials contain toxic lead or rare elements and often require costly thermal vacuum processing. Organic ferroelectric materials composed of light elements have advantages in this respect and could also be suitable for bio-compatible print production technologies for electronic devices. The ferroelectric polymer PVDF and its

related compounds are representative organic ferroelectric materials that operate at room temperature; solution processes such as spin-coating and micro- or nano-imprinting have been used to fabricate thin films with highly uniform thickness over a wide area. However, commercially available ferroelectric devices such as solid-state drives generally require an operating voltage below 5 V, and the fabrication of PVDF thin films to meet this demand involves many challenges.

Since the discovery of ferroelectricity in hydrogen-bonded compounds, these compounds have attracted much attention as future candidates for a crystalline organic ferroelectric material that provides a low  $E_c$  and high remnant polarization  $P_r$  near room temperature. In considering their application to electronic devices, it is important to fabricate thin films of organic ferroelectrics. Owing to its modest acidity and lack of polymorphs, we selected 2-methylbenzimidazole (MBI) [2] as a promising candidate for a chemically inert organic ferroelectric material for application in a low-cost printing process.

The fabrication of organic materials, including both polymers and small molecules, into thin-film devices by solution processing faces various challenges. Thin films for use in devices ideally form in a highly uniform shape and crystalline state. In contrast, organic molecules tend to form rough or inhomogeneous films from droplets due to random nucleation or the coffee-ring effect, and these films are prone to structural defects including pinholes or grain boundaries, causing leakage current, charge traps, and degraded device performance. Additionally, a ferroelectric thin film should have a polarization component normal to the substrate for capacitor structure devices. MBI is also advantageous here because it possesses

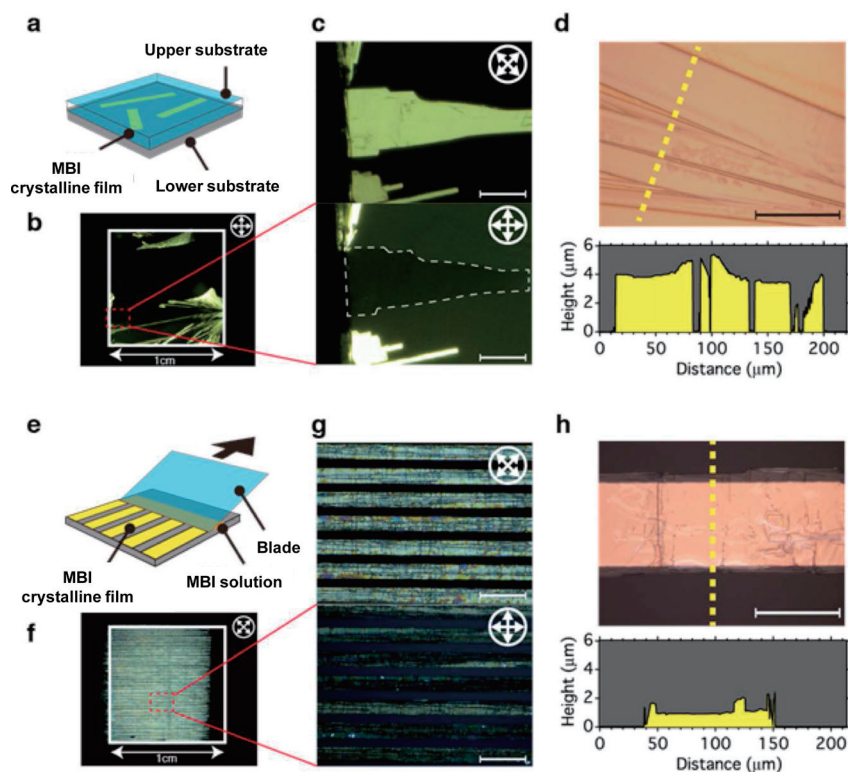
biaxial polarity in the pseudo-tetragonal crystal, so a polarization component normal to the film is more likely to emerge.

Single crystals of organic semiconductor thin films composed of small molecules have been obtained by several sophisticated techniques, such as dip-coating, inkjet printing, and solution shearing. Here we present the fabrication of crystalline organic ferroelectric thin films by a simple solution process for small molecules. By shearing a solution with a blade, plate-like single crystals of MBI possessing biaxial polarity were coated in a well-aligned orientation along a hydrophilic area on a silicon dioxide substrate.

First, we need to know the crystal growth characteristics and orientation of polarization axes on solid substrates. In employing spin-coating or inkjet printing, we found that droplets on a substrate surface inherently formed needle-shaped crystals instead of the desired thin-film plates, so we then examined the confined growth method. First, 2  $\mu\text{L}$  of a 1 wt% *N,N*-dimethylformamide solution of MBI was placed on the lower substrate, which was then covered by the upper substrate (Fig. 1a). After the solvent was evaporated through the gap for a few days, needles and elongated flake-like crystals were deposited at random positions on the substrate (Fig. 1b). In crossed-Nicols micrographs, each specimen exhibited homogeneous color changes from bright to dark upon rotation around an axis perpendicular to the substrate, suggesting a single crystal domain (Fig. 1c). Synchrotron X-ray diffraction measurements indicated that the longitudinal axis, namely, the fastest growth direction of the crystals, was parallel with the crystallographic *c* axis. In the optical image and the height profile measured with laser microscopy (Fig. 1d), we found continuous uneven surface structures 3–5  $\mu\text{m}$  in thickness, which were likely caused by the surface roughness of the upper substrate. Furthermore, a capacitor consisting of a flake-like crystal exhibits clear ferroelectric switching behavior.

Although this method occasionally provides a large, flat single crystal ( $\sim 0.5$  mm wide,  $> 1$  mm long), it is difficult to control the crystallization and obtain the desired thickness, size, and position.

To overcome this drawback, we combined hydrophilic/hydrophobic patterning and a solution shearing method for the fabrication of pinhole-free thin films with an arbitrary position, size, and shape. First, the surface of the  $\text{SiO}_2$  substrate was treated with hydrophilic/hydrophobic patterning consisting of a 100  $\mu\text{m}$  line and space (L/S) structure (Fig. 1e). An array of crystalline thin films can be successively formed by shearing the solution with a metal blade at a shearing speed of 25  $\mu\text{m}/\text{s}$ . Because the hydrophilic area confines the solution, the array of plate-like crystals grew along the long axis of the hydrophilic area ( $\sim 120$   $\mu\text{m}$  wide,  $\sim 1$  cm long) without forming voids (Fig. 1f). The thickness could be controlled between 0.5 and 5  $\mu\text{m}$  by changing the shearing speed and/or solution concentration. Simultaneous light extinction (Fig. 1g) by rotating cross-polarizers at  $\sim 45^\circ$  in the crossed-Nicols optical micrographs indicated a high degree of crystallographic alignment of these thin plate-like crystals. It should be noted that a single crystal domain occupied 68% of the total film area. Although the height profile showed



**Fig. 1:** Fabrication and morphology of thin MBI crystals. a–d) Aggregate of MBI flake-like crystals prepared between lower and upper silicon dioxide substrates by confined growth method. e–h) Array of plate-like MBI crystals grown on hydrophilic area of silicon dioxide substrate by solution shearing method.

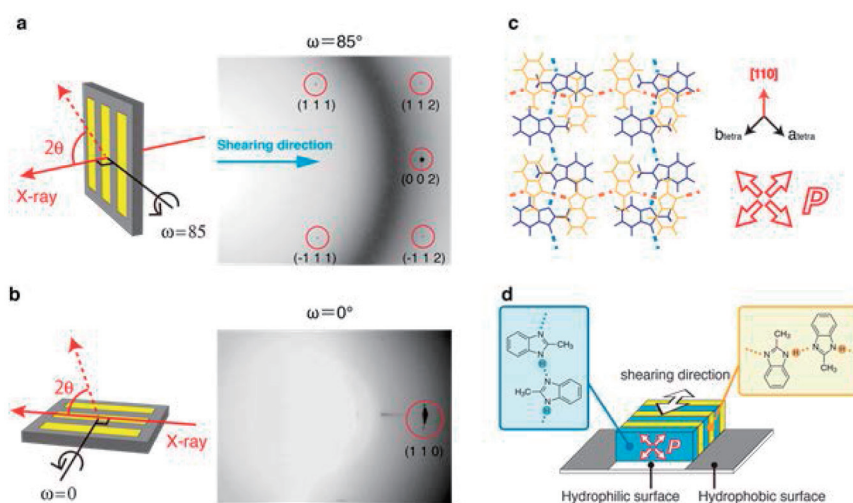
a terrace structure  $\sim 1\ \mu\text{m}$  in thickness except for a partial projection at the edge and inside the film (Fig. 1h) which was found to appear as a black line in crossed-Nicols images (Fig. 1g), full ferroelectric characterization can be achieved using these arrays of MBI plate-like crystals fabricated by solution shearing.

Without pre-patterning, needle-like crystals of width less than  $10\ \mu\text{m}$  were randomly grown very roughly along the shearing direction from the nucleation site. Therefore, the origin of the formation of uniform and continuous crystalline thin film is mainly attributed to the L&S pre-patterning treatment. The fraction of continuous film was evaluated under different hydrophilic pattern widths using the crossed-Nicols micrographs. The narrower pattern width improved the continuous nature of the films; the probability of obtaining single-crystal domains increased to as high as 96% using the  $50/50\ \mu\text{m}$  hydrophilic/hydrophobic pattern. We consider that the efficient outward flow within a droplet confined in the pattern is responsible for the pattern-width dependence. The solute molecules tend to precipitate in the vicinity of the droplet contact line because of the outward flow, which carries the solutes from the inside of the droplet toward the contact line. Outward flow should be accelerated in regions of high contact line curvature because of the increased Laplace pressure, by which solutes are effectively carried to the vicinity of a contact line. We consider that the improved crystallinity to obtain continuous films at narrower pattern width can be ascribed to the high curvature of the contact line that should permit efficient transportation and precipitation of the solute molecules, thus preventing the formation of voids within the films.

The lattice parameters and crystal orientations of the plate-like crystals were determined by synchrotron X-ray diffraction measurements. At a high incident angle ( $\omega = 85^\circ$ ), a single diffraction spot without any arc elongation suggested the formation of a single crystal (Fig. 2a). The proposed unit cell— $a = 13.876(7)\ \text{\AA}$ ,  $b = 13.930(6)\ \text{\AA}$ ,  $c$

$= 7.194(4)\ \text{\AA}$ ,  $\alpha = 90.152(10)^\circ$ ,  $\beta = 90.197(11)^\circ$ ,  $\gamma = 90.41(3)^\circ$ ,  $V = 1390(2)\ \text{\AA}^3$ —almost coincides with the pseudo-tetragonal lattice observed on the bulk MBI crystal [2] [ $a = b = 13.9639(3)\ \text{\AA}$ ,  $c = 7.2107(2)\ \text{\AA}$ ,  $V = 1406.02(6)\ \text{\AA}^3$ ]. The out-of-plane diffraction (Fig. 2b,  $\omega = 0^\circ$ ) shows the  $(110)_{\text{tetra}}$  reflection spot with arcs of diffracted intensity, implying that the in-plane direction of the crystal is slightly tilted relative to the substrate surface. Figures 2c and 2d show schematics of the molecular packing structure and crystal orientation on the substrate, respectively. In the pseudo-tetragonal unit cell, hydrogen-bonded chains are parallel with the  $[110]_{\text{tetra}}$  or  $[-110]_{\text{tetra}}$  direction (blue and orange dashed lines, respectively, Fig. 2c). Because the  $(110)_{\text{tetra}}$  diffraction spot was observed in the direction perpendicular to the substrate surface, one of the hydrogen chains is directed perpendicular to the substrate surface. Additionally, the appearance of the  $(002)_{\text{tetra}}$  spot in the in-plane diffraction image (Fig. 2a) indicates that the  $c$  axis is parallel with the shearing direction, and the polar proton ordering  $(001)_{\text{tetra}}$  plane stands perpendicular to the substrate surface. These results provide unambiguous evidence that the ferroelectric polarization has a component perpendicular to the substrate; this feature is indispensable for fabricating ferroelectric devices such as data storage memory.

We found that the normal component of the ferroelectric polarization is switchable by applying a small voltage ( $< 5\ \text{V}$ ). Figure 3a displays typical electric polarization ( $P$ ) and current ( $I$ ) versus



**Fig. 2:** Determination of crystal orientation by synchrotron-radiated X-ray diffraction. Oscillation photographs of plate-like crystal obtained by solution shearing method for high-incident-angle diffraction (a), and out-of-plane diffraction (b), where  $\omega$  is the incident angle. c) Schematic of molecular packing. d) Schematic of molecular chain alignment on substrate surface.

electric field ( $E$ ) hysteresis loops of  $[110]_{\text{tetra}}$  polarization measured at room temperature with a triangular ac electric field of various frequencies (10–1,000 Hz). The plate-like crystal capacitor exhibited typical ferroelectric features, as demonstrated by the quasi-rectangular loops and the corresponding peak in the displacement current. The pristine capacitor shows an  $E_c$  value of  $\sim 20 \text{ kVcm}^{-1}$  and a remnant polarization  $P_r$  of  $\sim 2.5 \mu\text{Ccm}^{-2}$  at 10 Hz, which is comparable to those of bulk MBI crystal ( $E_c \sim 15 \text{ kVcm}^{-1}$ ,  $P_r \sim 5 \mu\text{Ccm}^{-2}$  at 2 Hz). Polarization switching of the 1.4- $\mu\text{m}$ -thick film appeared at a very low voltage of about 3–4 V at 10 Hz. This voltage is much lower than those of ferroelectric polymers such as P(VDF-TrFE) (ca. 30–40 V for 0.5- $\mu\text{m}$ -thick films). With increasing ac frequency,  $P_r$  decreased and  $E_c$  increased.

The fatigue characteristics were evaluated by plotting the normalized  $E_c$  and  $P_r$  as a function of the cumulative number of cycles (Fig. 3b). Here, a bipolar rectangular wave voltage of  $\pm 15 \text{ V}$  and a frequency of 10, 100, or 1,000 Hz was applied. The film did not show wake-up behavior of  $P_r$ , i.e.

increasing polarization with continuously repeated switching.

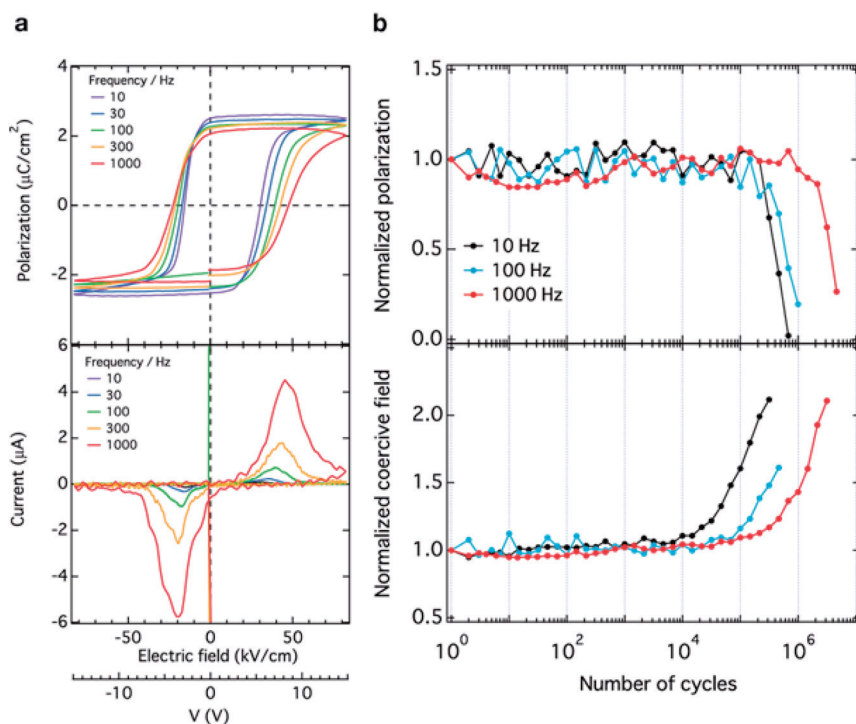
For the practical application of ferroelectric materials, the top priority is to control the polarization orientation and the operation of polarization reversal at low voltages. It is demonstrated that the combination of MBI and solution shearing method with hydrophilic/hydrophobic L&S patterned surface can meet these requirements. The material is also rather stable at ambient conditions. The use of small-molecule-based crystalline materials may suffer from brittleness or sublimability. However, these issues could be overcome by using thinner films, solution-processed top electrodes, and also protective layers to cover the crystal surfaces, which may allow us to take full advantage of the inherent low operating voltage and high remnant polarization characteristics of the MBI.

In summary, we have developed a simple method of fabricating organic ferroelectric thin films composed of the small molecule MBI by a solution process. By shearing the solution droplets on a substrate with a blade, an array of single-crystalline films of MBI can be successively

deposited along a predefined hydrophilic patterned surface. We successfully aligned the in-plane molecular orientation and out-of-plane orientation of the polarization. The capacitor device structure exhibited a quasi-rectangular  $P$ – $E$  hysteresis loop with a switching voltage of 3–4 V at room temperature. We think this method holds promise for realizing print production technology for bio-compatible, environmentally friendly, and flexible ferroelectric devices.

## References

- [1] Y. Noda, T. Yamada, K. Kobayashi, R. Kumai, S. Horiuchi, F. Kagawa, T. Hasegawa, *Adv. Mater.* 2015, **27**, 6475–6481.
- [2] S. Horiuchi, F. Kagawa, K. Hatahara, K. Kobayashi, R. Kumai, Y. Murakami, Y. Tokura, *Nat. Commun.* 2012, **3**, 1308.



**Fig. 3:** Ferroelectric properties of thin film fabricated by solution shearing method. All measurements were conducted at room temperature for a capacitor structure on a 1.4- $\mu\text{m}$ -thick film with electrode contact area of  $100 \times 100 \mu\text{m}^2$ . a) Electric polarization (top) and displacement current (bottom) versus electric field hysteresis loops of  $[110]_{\text{tetra}}$  polarization with a triangular ac electric field of various frequencies ( $f = 10$ –1,000 Hz). b) Fatigue characteristics: normalized  $E_c$  (top) and  $P_r$  (bottom) in the first cycle as a function of the logarithm of the number of cycles. Applied voltage was fixed at  $\pm 15 \text{ V}$  with a rectangular waveform, the frequency of which varied from 10 Hz to 1 kHz.