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Study of charge state of polarization domain walls in organic ferroelectric 2-methylbenzimidazole crystals

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Nowadays, there is an active search [1] of organic and semi-organic, environmentally safe and biocompatible ferroelectric materials that do not contain lead and heavy metals.

2-methylbenzimidazole (MBI) can be considered as a promising chemically inert organic ferroelectric [2]. The crystal structure of MBI has pseudosymmetry and is described by the tetragonal space group $P4_2/n$ (real group Pn [3]). Dielectric hysteresis loops were observed for electric fields perpendicular to the pseudotetragonal axis in MBI crystals. The spontaneous polarization and coercive field at room temperature were $P_s \sim 5$ μC/cm^2 and $E_c \sim 3$ V/μm at a frequency of $\nu = 30$ Hz [2].

Domain structures were observed at the surface of MBI crystal using piezoresponse force microscopy (PFM) [3]. The observed PFM contrast interpretation given by the authors implied the continuity of the normal polarization at a domain wall. This is equivalent to uncharged domain walls.

We applied atomic force microscopy (AFM) to investigate MBI crystalline samples. We found out that the samples were rather soft, Young module was less than 1 GPa. This complicated the contact probing the sample's polarization domain structures. Therefore we used non-contact AFM modes: Kelvin-probe force microscopy (KPFM) and electrostatic force microscopy (EFM). This permitted us to observe cross-hatched patterns of the surface potential relief that may be related to the polarization distribution.

We studied two types of MBI samples: single crystals, Figure 1, and microcrystalline films, Figure 2. The single crystals were fabricated from a solution of MBI powder in ethanol by evaporation and slow cooling method. The films were formed by the deposition of MBI from the ethanol solution onto Pt coated Si substrates [2].

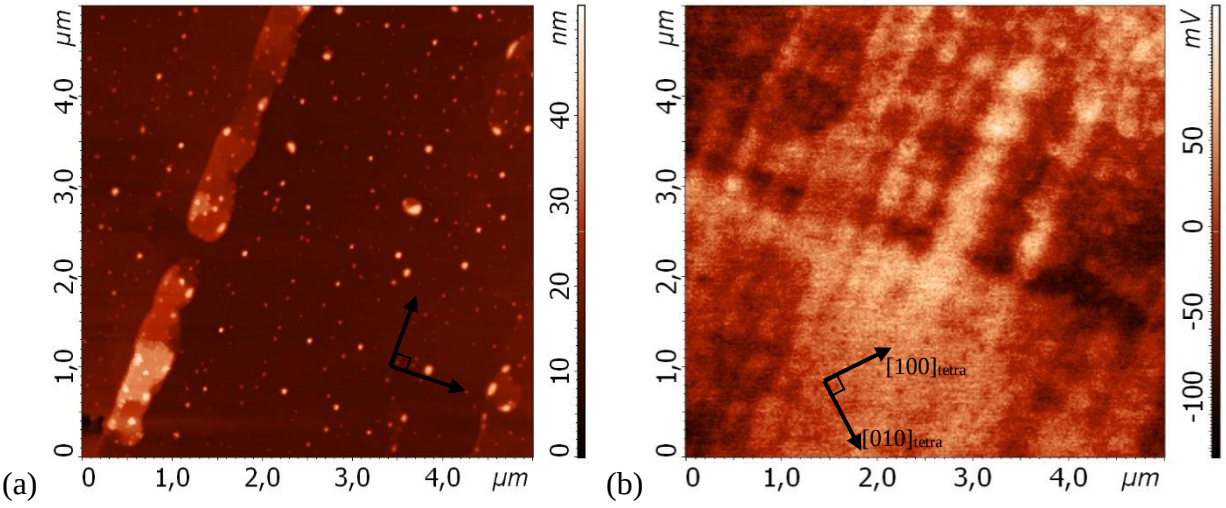

Figure 1. Taping mode AFM topography image (a) and simultaneously obtained surface potential map (b) of the MBI single crystal surface. Parameters of visualization: soft CSG10 probe with a resonant frequency of 29,9 kHz and free / set point oscillation amplitude of about 9 nm / 5 nm; probe-sample distance at KPFM mode is about 13 nm. The crystallographic directions are shown by arrows; pseudotetragonal axis is perpendicular to the figure plane.

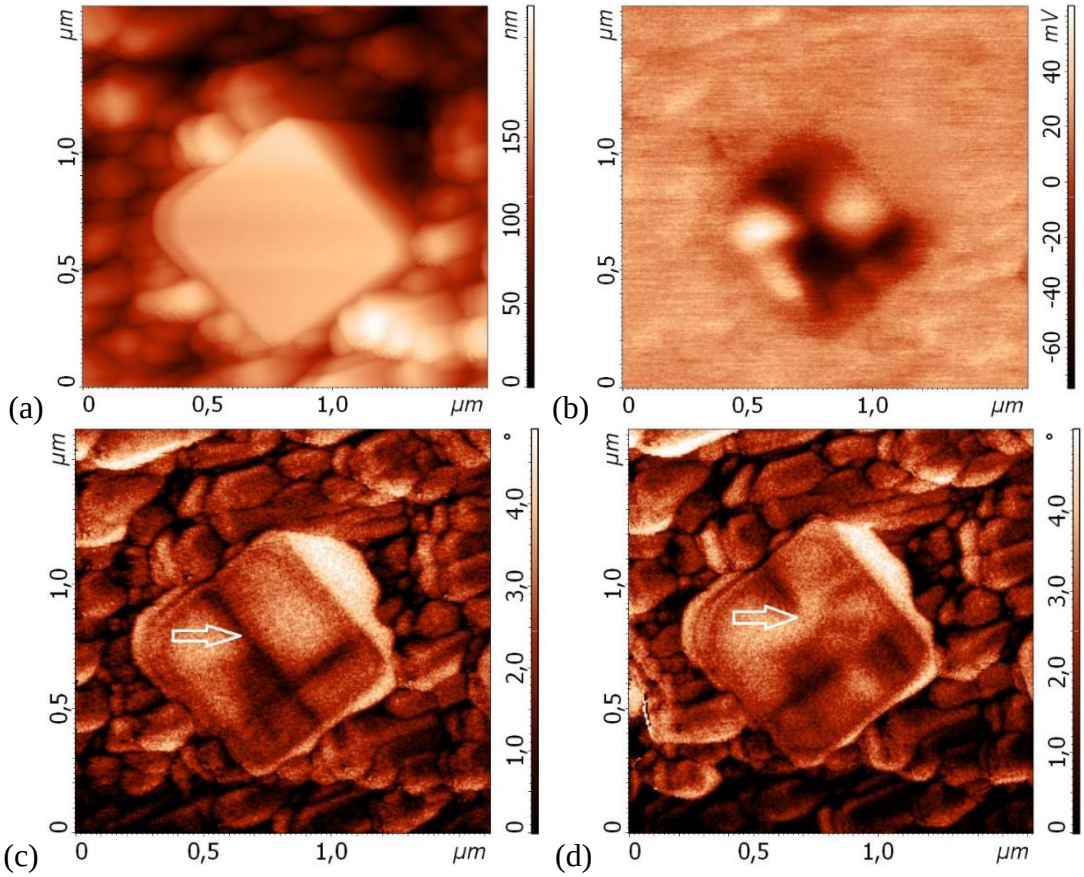

Figure 2. Taping mode AFM topography image (a) and simultaneously obtained surface potential map(b) of the MBI film on Pt coated substrate; EFM images before (c) and after (d) square voltage pulse application (τ = 6 s, U = 3 V). Parameters of visualization: fnp01Pt with a resonant frequency of 123 kHz and free / set point oscillation amplitude of about 9 nm / 8 nm; average probe-sample distances both at KPFM and EFM mode are about 8 nm, free amplitude oscillations at EFM mode is 4,5 nm. Arrows indicate the place the pulse was applied.

The amplitude of surface potential variations for the single crystal in Figure 1b is of order of 100 mV, while the spatial scale of these variations is about 100 nm. Hence, the characteristic in-plane electric field is 10 KV/cm and, accordingly, the charge density at the domain wall is about 1 nC/cm^2. Rectangular flat flakes were found on the film (Fig. 2a). The surface potential morphology at the flake (Fig. 2b) is similar to the pattern observed for the single crystal (Fig. 1b). It was possible to modify the spontaneous domain structure of the flake (Fig. 2c,d).

Our study is still in progress. It is planned to carry out combined KPFM, EFM and PFM investigations of both samples.

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