Polymorphic phase transitions and ferroelectric properties in β-glycine single crystals and micro islands

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Crystalline structures based on vital biological molecules (amino acids, peptides, DNA) demonstrate nonlinear optical, piezoelectric, and ferroelectric properties similar to their inorganic counterparts [1-4]. Recently observed room-temperature ferroelectricity [5] and high shear piezoelectricity [6] in β-glycine opens up new perspectives of using this material in biocompatible non-volatile memories, optical switches, transistor gates, nonlinear optical and piezoelectric devices. At ambient conditions glycine crystallizes in three polymorphic phases: α, β and γ [7], only β-phase possesses both piezoelectric and ferroelectric properties. Metastable β-phase can irreversibly transform into the γ or α-phases under the presence of moisture [7]. The microscopic mechanism of such transformation still requires detailed investigations. With the continuing demand for miniaturization of ferroelectrics it is becoming extremely important to scale down their dimensions and to form arrays of self-organized micro- and nanocrystals.

In the present work we demonstrate the β→γ polymorphic transformation in glycine single crystal in situ visualized by piezoresponse force microscopy (PFM). Transformation into γ-phase was visualized during gradual decreasing of relative humidity from 30 down to 25%. It was shown that the transformation occurs for relative humidity above 25%. Analysis of the time dependence of ratio β to γ phase area obtained from PFM images allowed to reveal the averaged velocity of the phase boundary motion. Raman analysis of the phase boundary allowed to provide a microscopic model of the process.

The faceted crystals with in-plane polar axis were grown from aqueous solution via drop drying on Pt/SiO/Si substrate in air with controlled relative humidity. The detail experimental study of the neutral and charged domain walls in β-glycine microcrystals using atomic force (AFM) and PFM was performed using scanning probe microscopes Ntegra Aura (NT-MDT, Russia) and Asylum MFP 3D SA (Asylum Research, USA).

Three types of as-grown domain structure were found: (1) striped domains with flat charged domain walls (Fig. 1a), (2) quasiperiodic ensembles of submicron width needle domains (Fig. 1b) and (3) large area domains with irregular shaped domain walls (Fig. 1c). The formation of as-grown domain structure with flat charged domain walls and a smooth change in orientation near the crystal edges can be attributed to growth layers located perpendicular to the polar axis and representing a periodic change in the composition or concentration of impurities [8,9]. The polarization direction is determined by the gradient sign of the composition or concentration, so the domain walls are localized at the places where the gradient sign changes. The formation of two other types of the as-grown domain structure can be attributed to switching the polarization in the striped domains under the action of the pyroelectric field E_{pyr}, which appears when the temperature of the crystal changes [9].

The shallow wells of 0.2-1 nm-depth and about 150 nm-width were revealed along the charged walls. The formation of these features was attributed to selective etching by water layer appeared at the surface in humid air. In contrast the pits appeared at neutral domain walls are due to deformation of the crystal lattice in the vicinity of the wall.

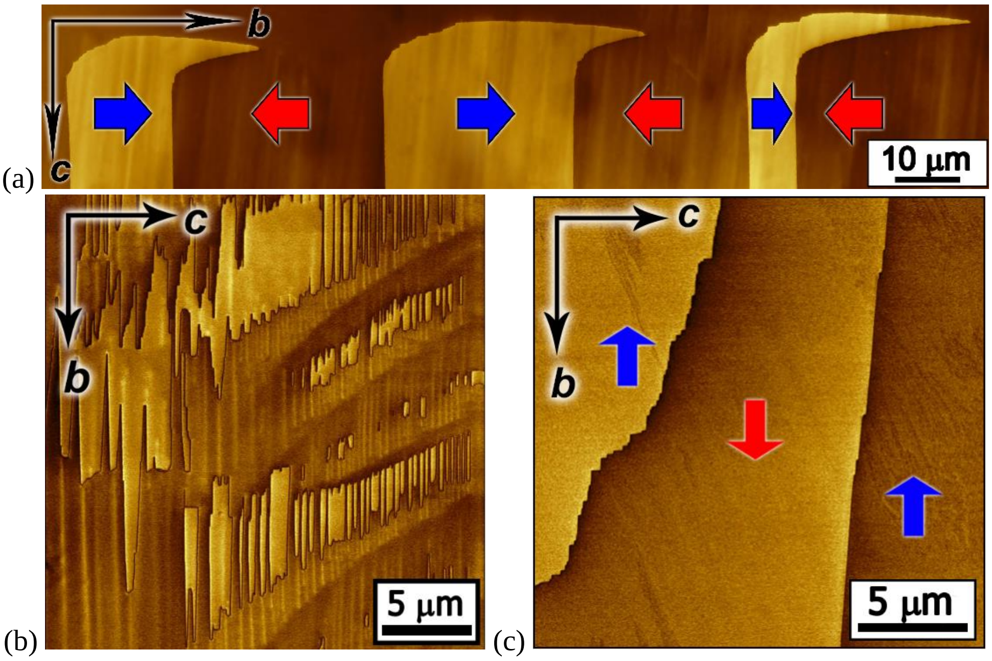

Figure 1. Lateral PFM images of the as-grown domain structure types: (a) striped domains with flat charged domain walls, (b) quasiperiodic ensembles of submicron width needle domains, (c) large area domains with irregular shaped domain walls.

In this work spin-coating formation of self-organized β-glycine films is also presented. The morphology of the obtained films varied from feather-like structures to quasi-regular arrays of individual micro- and nanoislands and nanowires. Micro- and nanoislands are oriented in a radial direction from the center of "grains" formed during evaporative dewetting. The kinetics of the dewetting follows the $t^{-1/2}$ law, which is responsible for the observed polygon shape of the grain boundaries [10]. It was confirmed by confocal Raman microscopy that all the structures belonged to ferroelectric β-phase and possess high stability.

Piezoelectric properties and domain structure of the films were studied by PFM. It was shown that ferroelectric polarization in β-glycine islands is parallel to the substrate and switchable under a relatively small bias applied by the conducting tip of piezoresponse force microscope.

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