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A continuum model on the nanomesa and nanowell formation in Langmuir–Blodgett ferroelectric polymeric films

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Abstract

Spontaneous crystalline nanomesa and nanowell formation has recently been discovered in polyvinylidene fluoride trifluoroethylene [P(VDF–TrFE)] copolymer films developed by Langmuir–Blodgett (LB) deposition. In this paper, we propose a continuum field model to analyze this remarkable phenomenon, consisting of kinematics, energetics, and kinetics of pattern formation and evolution in P(VDF–TrFE) films. Linear perturbation analysis has been carried out to analyze the stability and growth of patterns under small perturbations, and finite difference numerical simulations have been implemented to simulate the morphologies and evolutions of nanomesas and nanowells. The effects of film thickness and a number of other material parameters have been considered in our simulations, which agree well with experimental observations. We expect that our modeling and simulation methods can be used to guide the design and optimization of nanomesa and nanowell patterns for technological applications.

Keywords: Self-organizing; Pattern formation; Nanomesa; Nanowell; Ferroelectric polymer

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1. Introduction

Polyvinylidene fluoride (PVDF) is a non-conjugated fluorinated hydrocarbon polymer with a simple linear sequence of molecular structure $-(CH_2-CF_2)_n-$ (Lovinger, 1983; Tashiro, 1995). The all-trans TTTT conformation is one of the basic forms of PVDF polymer chains, and the alternating trans-gauche TGT$\bar{G}$ conformation is also common, with G/$\bar{G}$ denoting $\pm 60^\circ$ rotation of the dihedral bond. Additional ordered conformations in PVDF include the helical conformation TGTG and longer repeating sequence TTTG. These polymer chains usually are organized in crystalline lattices, among them the paraelectric α phase, in which the dipole moments of the alternating trans-gauche conformation cancel each other out, and ferroelectric β phase, where the dipole moments of the all-trans conformation lead to macroscopic polarization. To control the phase transition temperature of β phase, random copolymer of PVDF and trifluoroethylene (TrFE) has been developed (Tashiro, 1995).

A remarkable phenomenon of spontaneous crystalline nanomesa and nanowell formation has recently been discovered in P(VDF–TrFE) copolymer films developed by Langmuir–Blodgett (LB) deposition. After annealing an initially uniform one monolayer (ML) film at 125 °C for 1 h, an array of predominately disc-shaped nanomesas isolated from each other on the substrate appears, with average diameter 95 ± 22 nm and average thickness 8.7 ± 0.4 nm (Bai and Ducharme, 2004); see Fig. 1 for the atomic force microscopy (AFM) image. The nanomesas are ferroelectric, with the same crystalline orientation and nearly the same transition temperature found in a continuous film (Bai and Ducharme, 2004; Bune et al., 1998). As the number of the monolayers increases, more nanomesas develop, some joined into extended shapes, and tending toward percolation as the number of nanomesas increases. The 4-ML films are mostly filled in, resulting in a complementary pattern of nanowells with diameter 128 ± 37 nm and thickness 9.8 ± 3.3 nm. At 8-ML and thicker, the films remain continuous without nanowells, even

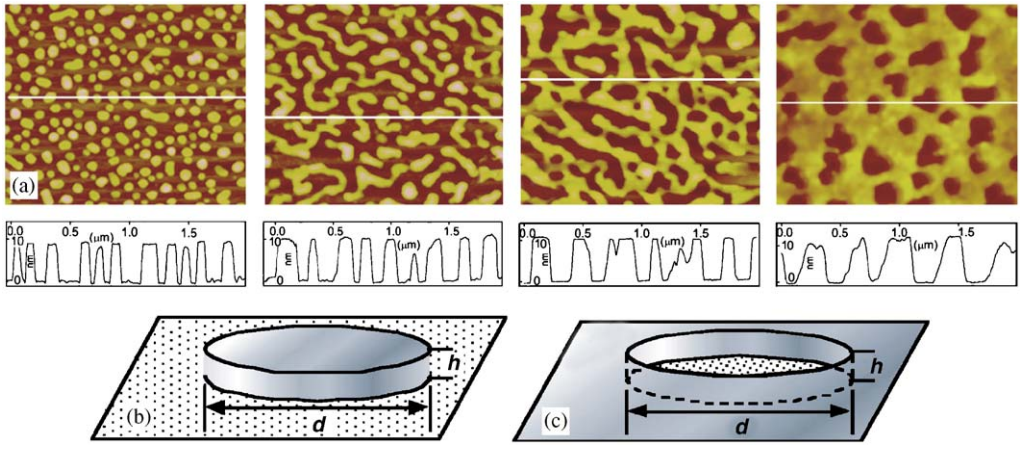

Fig. 1. Images of nanomesa and nanowell obtained by annealing uniform thin films of thickness, L–R, 1, 2, 3, and 4 ML. Below each image is a height profile recorded along the white line in the image. (a) Room temperature AFM images, and associated height profiles from P(VDF–TrFE) copolymer LB films; (b and c) schematic illustration of nanomesa and nanowell.