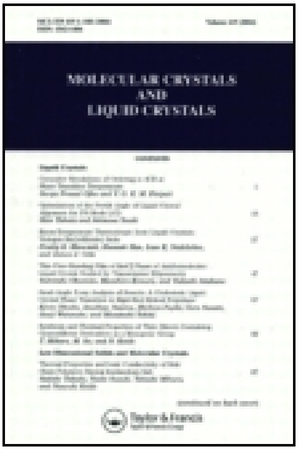

# Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

# Characterization of Nanoscale Domains in Ferroelectric Polymer Thin Films by Scanning Probe Microscopy

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# Characterization of Nanoscale Domains in Ferroelectric Polymer Thin Films by Scanning Probe Microscopy

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Nanoscale domains have been formed and detected in ferroelectric polymer thin films using scanning probe techniques. The "erasing" and "rewriting" of local domains are also demonstrated and discussed in this article. The results suggest that ferroelectric polymer is a promising ultrahigh-density information storage medium.

*Keywords*: ferroelectric domain; poling; erasing; rewriting

## INTRODUCTION

Ferroelectric materials have attracted a wide range of interests due to its remarkable electrical properties. A combination of the ferroelectric material with scanning probe technique was realized by Güthner and coworkers, who first reported the formation and visualization of local polarized domains in organic ferroelectric thin films using modified atomic force microscope (AFM)[1]. Hidaka et al. and Gruverman et al. have also studied inorganic ferroelectric films using this technique[2,3]. The formation of local domains and their surface characteristics of ferroelectric polymer thin films were also described in the previous reports[4,5].

In this present work, we use this technique to form nanoscale domains in ferroelectric polymer thin films. The erasing and rewriting of nanoscale domains are also demonstrated.

## EXPERIMENTAL SECTION

The copolymer of vinylidene fluoride (VDF) and trifluoroethylene (TrFE), as ferroelectric polymer, was used in this work. The VDF/TrFE copolymer in a 73/27 ratio was dissolved in methyl ethyl ketone with about 0.5% weight concentration. The highly ordered pyrolytic graphite (HOPG) as a conductive substrate was prepared by cleaving in air. The fabrication of samples and the formation of local domains were described in references [4] and [6].

## RESULTS AND DISCUSSION

Figure 1 shows the morphology of the ferroelectric copolymer film on graphite substrate. The surface consists of rod-like grains, which is often seen in the polymer films. The topographic image indicates that the film consisting of the grains has very high crystallinity. According to the previous results[6-8], The molecular chains fold in the plane parallel to the substrate and form a "re-entry" structure in the rod-like grains. The F-H dipoles are normal to the molecular chains. When the samples have this kind of structures, they can be well polarized owing to their high crystallinity.

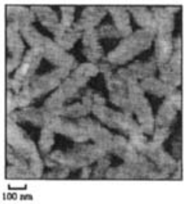

Fig.1 AFM Topographic image of P(VDF/TrFE) thin film on graphite substrate.

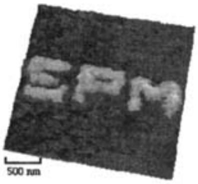

Fig.2 Piezoresponse image of "SPM" pattern domain formed by vector scanning the probe tip.

In order to form a complex pattern domain, the tip was vector scanned on the surface of the film with a sample bias of DC 8 V at a scanning rate of 500 nm/sec. A pattern of "SPM" was formed as shown in Fig. 2. The piezoresponse image clearly shows the formed domain. Measurements of the topography after this domain formation confirmed that no measurable morphological changes were made on the film. Because the polymer film has a soft surface, an AFM tip with a small spring constant is necessary to avoid damages on the surface. A Cr/Au-coated silicon nitride AFM tip with a typical spring constant of 0.1N/m was used in this present work.

Figure 3(a) shows a piezoresponse image of the polymer film with eight poled domains. The durations of the applied pulse voltages were 0.05, 0.1, 0.5, and 1 sec from the left to the right in the upper half, and 2, 4, 6, and 8 sec from the left to the right in the lower half, respectively. The applied voltage was 8 V for each poling.

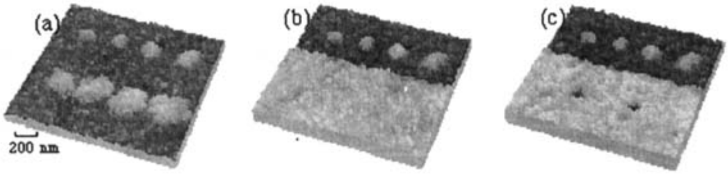

Fig.3(a) Piezoresponse image of local domains with different poling pulse durations. (b) Erasing of the lower domains with a sample bias of 10 V. (c) Formation of two new domains in the lower half by applying pulse voltage of –8 V, 0.1sec.

In order to erase the local domains, the tip was scanned on the lower half of the surface with a sample bias of 10 V. The piezoresponse image of the same area is shown in Fig. 3(b). It can be found that the lower four domains were erased through the re-poling process. Then another two pulses with the voltage of -8 V and the duration of 0.1 sec were applied on the lower half area and two new domains were rewritten (shown in Fig. 3(c)).

The changes in the piezoresponse images shown above are attributed to the orientation and switching of the dipoles in the ferroelectric films. By locally poling only local dipoles could be aligned. We could visualize the local domains since it had different piezoresponse from the background. When the lower half of the surface was scanned with a high bias, the local domains in the lower half could not be detected because the lower area had the same piezoresponse. Therefore, the local domains were regarded as "erased". When reverse pulse voltages were applied to the film by a probe tip, the local dipoles were re-switched. The new domains show the piezoresponse with the opposite phase with respect to the background area so that they can be differentiated. The result shows that the nanoscale domains can be "erased" and "rewritten" easily. The erasing and rewriting process was repeated many times. The ferroelectric polymer film demonstrated outstanding polarization features.

## SUMMARY

Formation of nanoscale domains in the ferroelectric polymer thin films was demonstrated by using the scanning probe technique. The erasing and rewriting of local domains were also realized. The result shows that the ferroelectric polymer film can be a potential erasable ultrahigh-density recording medium.

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