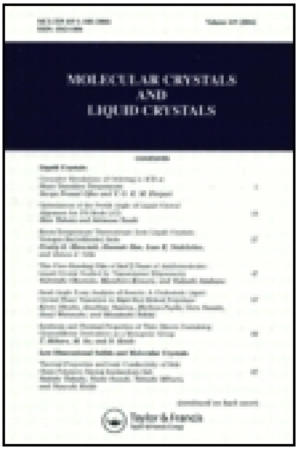

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Formation of Nanoscale Polarized Domains in Organic Ferroelectric Thin Films by Scanning Force Microscopy

Xinqi Chen [a], Hirofumi Yamada [a], Toshihisa Horiuchi [a], Kazumi Matsushige [a] & Paul S. Weiss [b]

[a] Department of Electronic Science and Engineering, Kyoto University, Kyoto, 606-8501, Japan

[b] Department of Chemistry, 152 Davey Laboratory, The Pennsylvania State University, University Park, PA, 16802-6300, USA

To cite this article: Xinqi Chen, Hirofumi Yamada, Toshihisa Horiuchi, Kazumi Matsushige & Paul S. Weiss (1999): Formation of Nanoscale Polarized Domains in Organic Ferroelectric Thin Films by Scanning Force Microscopy, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 337:1, 285-288

To link to this article: http://dx.doi.org/10.1080/10587259908023433

Mol. Cryst. and Liq. Cryst., 1999, Vol. 337, pp. 285-288
Reprints available directly from the publisher
Photocopying permitted by license only

Formation of Nanoscale Polarized Domains in Organic Ferroelectric Thin Films by Scanning Force Microscopy

XINQI CHEN[a], HIROFUMI YAMADA[a], TOSHIHISA HORIUCHI[a], KAZUMI MATSUSHIGE[a] and PAUL S. WEISS[b]

[a]*Department of Electronic Science and Engineering, Kyoto University, Kyoto 606–8501, Japan and* [b]*Department of Chemistry, 152 Davey Laboratory, The Pennsylvania State University, University Park, PA 16802–6300, USA*

Scanning force microscopy was used to form nanometer-scale domains in P(VDF/TrFE) thin films by applying voltage pulses between a gold-coated cantilever and a conductive substrate. We demonstrated that a domain can be switched by applying a voltage with the opposite polarity. These results indicate that this ferroelectric copolymer is a promising material for high-density data storage.

Keywords: P(VDF/TrFE); ferroelectric; domain; polarization; dipole; SFM

INTRODUCTION

Scanning tunneling microscopy and related scanning probe techniques have been successful in revealing nanometer-scale and even atomic-scale structures and properties[1,2]. In addition to high-resolution imaging of surfaces, they are powerful tools for surface modification that can be utilized for fabrication and testing of high-density electronic devices. One promising route is to induce local changes in electrical properties for high-density data recording. In particular, creation and detection of local ferroelectric domains by scanning force microscopy (SFM) have gained much attention as means to achieve high-density rewritable recording[3-9].

In the present work, a scanning probe technique based on piezoelectric modulation of ferroelectric thin films was used to study local polarized domains of the copolymer of vinylidene fluoride (VDF) and trifluoroethylene (TrFE), referred to as P(VDF/TrFE). Local polarized domains with a diameter of less than 100 nm were formed and detected on the organic ferroelectric thin films by scanning force microscopy. We also demonstrated that local domains could be switched.

EXPERIMENTAL

The VDF/TrFE copolymer with a molar content ratio of 73/27 was used in this work. The P(VDF/TrFE) thin films were prepared by spin-coating method, depositing on a graphite substrate, and then annealing at 140°C for four hours. The thickness of the thin film is about 20 nm, as measured by line profiles of a SFM topographic image.

A commercially available scanning probe microscope (Seiko Instruments, SPI 3800) was used. In order to acquire both topographic images and piezoelectric response image simultaneously, we used a gold-coated Si_3N_4 cantilever with a spring constant of 0.75 N/m. By applying a small oscillating potential between the tip and the graphite substrate while the tip scanned a local polarized area in contact with the film, the resulting piezoelectric vibration was able to be detected with a lock-in amplifier and recorded by the control electronics. Figure 1 shows a schematic diagram of the modified SFM setup.

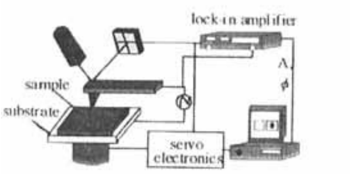

FIGURE 1 A schematic diagram of the modified SFM setup.
See Color Plate VIII at the back of this issue.

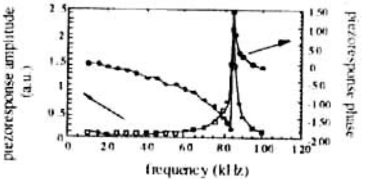

FIGURE 2 The frequency spectra of the piezoresponse amplitude and the phase.
See Color Plate IX at the back of this issue.

RESULTS AND DISCUSSION

The frequency dependencies of the piezoresponse amplitude and the phase were investigated and the results are shown in Figure 2. The figure shows that the conductive tip in contact with the thin film has a resonant frequency of about 86 kHz. In order to enhance the measuring sensitivity, the piezoresponse images were taken by applying the oscillating voltage at a frequency of 80 kHz. The contrast of the piezoresponse images at this because it is close to this resonance. It should be noted, however, that the piezoresponse phase was delayed nearly 180° in this case.

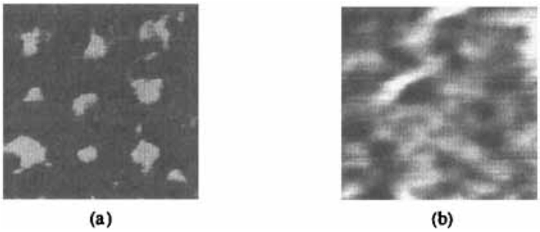

FIGURE 3 Simultaneously recorded images of a P(VDF/TrFE) film (scan area: 600nm x 600nm): (a) piezoresponse, and (b) topography.

See color plate X at the back of this issue.

Figure 3(a) is a piezoresponse image of a local polarized area and (b) is a topographic image taken simultaneously. In figure 3(a), there are nine dots each of which were "written" by applying single negative pulses of -12V with a duration of 20 ms. No topographic change can be found in figure 3(b) due to this poling. Therefore, these dots reflect the polarization changes in the ferroelectric thin film. Figure 4 shows a schematic diagram for inducing the polarization change -- orienting the dipole and thereby inducing a high local piezoelectric effect. The average diameter of the local domains in figure 3(a) is less than 100 nm, corresponding to a recording density of 2.5 Gbit/cm^2.

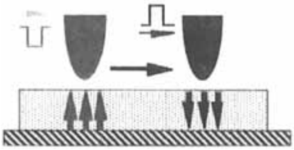

FIGURE 4 A schematic diagram of local poling by the conductive tip.

See color plate XI at the back of this issue.

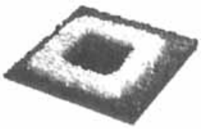

FIGURE 5 The piezoresponse image of a large-scale poled area (scan area: 6μm x 6μm).

See color plate XII at the back of this issue.

Polarization switching on a micron-scale in the P(VDF/TrFE) thin film is shown in figure 5. The conductive tip scanned an area of 4μm x 4μm under a -10V bias and then scanned the central area of 2μm x 2μm with a +10V bias. The outer bright region represents the negative domain where the film polarization is oriented away from the substrate, while the inner dark region corresponds to the positive domain where the dipole is oriented toward the substrate. The result also shows that the initially poled area was easily repoled in the opposite direction. Thus, the nanoscale dots shown in figure 3(a) can be switched by applying voltage pulses with the opposite polarity. The minimum size of local polarized domains is strongly dependent on the thickness of ferroelectric layers[8]. A. V. Bune et al suggested that these organic materials can maintain the ferroelectricity until the film thickness is reduced to a few nanometers[10]. Therefore, ultrathin ferroelectric copolymer films are expected to be useful as ultrahigh-density data storage media.

CONCLUSIONS

We have demonstrated that the SFM was a powerful tool for forming and mapping nanometer-scale domains in ferroelectric copolymer thin films. We created local polarized domains with diameters of less than 100 nm by applying pulses across the films. The polarized domains were switched by applying voltage pulses with the opposite polarity, indicating that the nanoscale domains are "erasable". We thus suggest that such organic ferroelectric thin films are promising candidates for high-density recording media.

Acknowledgments

The support of Kyoto University Venture Business Laboratory (KU-VBL) and a grant-in-aid from the Ministry of Education, Science, Sports and Culture of Japan are gratefully acknowledged.

References

[1] G. Binnig et al, Appl. Phys. Lett., **40,** 178 (1982).

[2] G. Binnig et al, Phys. Rew. **Lett., 56,** 930 (1986).

[3] P. Güthner and K. Dransfeld, Appl. Phys. Lett., **61,** 1137 (1992).

[4] K. Franke et al, Surf. Sci. Lett., **302,** L283 (1994).

[5] A. Gruverman, O. Auciello and H. Tokumoto, J. Vac. Sci. Technol., **B14,** 602 (1996).

[6] T. Hidaka et al, Appl. Phys. Lett., **68,** 2358 (1996).

[7] X. Q. Chen, H. Yamada, T. Horiuchi and K. Matsushige, Jpn. J. Appl. Phys., **37,** 3834 (1998).

[8] X. Q. Chen. Y. Terai. T. Horiuchi, H. Yamada, K. Matsushige and P. S. Weiss, submitted to Thin Solid Films.

[9] K. Matsushige, H. Yamada, H. Tanaka, T. Horiuchi and X. Q. Chen., Nanotechnology, **9,** 208 (1998).

[10] A. V. Bune et al, Nature, **391,** 874 (1998).