POLAR ORGANIC AND FERROELECTRIC SURFACES

Liquid/Air and Solid/Air Interface Inspection by Submarine Scanning Force Microscopy and Linear and Non-Linear Optical Microscopy

Ch. Seuret, H. Looser and L. Eng

The Langmuir-Blodgett (LB) film technique consists of a layer by layer transfer of organic compressed monolayers floating on a liquid subphase onto a solid substrate. LB films are one approach to fabricate waveguides for integrated frequency-doublers. Synthesis of specific chromophores results in a non-centrosymmetric structure necessary for second-harmonic generation. In contrast to deposition like melt-spinning or organic molecular deposition by beam epitaxy, the LB technique offers the advantage of thickness control of individual monolayers. On the other hand, because of the very small van der Waals interaction between the LB molecules and the substrate material, this method presents disadvantages like film instability.

We have developed different techniques to study the behaviour of LB molecules during the compression on the water subphase and after film transfer onto solid substrates. Far-field optical methods like absorption-enhanced contrast microscopy or second-harmonic microscopy as well as atomic force microscopy (AFM) in both contact and non-contact modes have been used to characterize Langmuir as well as Langmuir-Blodgett films. A special force microscope has been developed in order to investigate the LB molecules when floating on the water surface. This submarine AFM (SAFM) is constructed as a stand-alone, remote-controlled and water-tight microscope that can be put into the water subphase upside down. The SAFM[1] provides both HR images of the floating Langmuir films and force interaction curves perpendicular to the interface.

We investigate three kinds of LB molecules (C218, SNBD, DCANP), which are build-up of three different chromophores. The shape of solid domains for all three molecules as well as their phase diagrams are different: we observe needle shaped domains for SNBD, spherulites for DCANP, and a branched structure for C218. Optical and force microscopy inspect both the structural and optical properties of these LB films, from which the molecular orientation and the intermolecular interactions may be deduced. As an example, our measurements on SNBD films confirm that the hydro-carbon chains are aligned on a straight line, which, in solid domains, attaches perpendicular to the substrate surface.

Reference: L.M. Eng, Ch. Seuret, H. Looser and P. Günter, *J. Vac. Sci. Techn.* ***B14*** *(1996) 1386.*

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Characterization of Molecular Crystals by Scanning Force Microscopy

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Organic material with large second-order nonlinear optical susceptibilities are of interest because of their potential applications in optical signal processing and frequency conversion; crystal growth technique is one possibility to fabricate non-centrosymmetric structures with large nonlinear optical coefficients. It has been found, that the electro-optical response amplitude dependent strongly on the crystal quality[1]. Here, we investigated non linear optical (NLO) organic crystals with scanning force microscopy (SFM) in order to reveal both macroscopic and molecular surface features. Such an inspection is necessary to improve the crystal quality. Operation of the SFM in different measuring modes allows several properties to be deduced: contact SFM reveals the surface topography of the NLO crystals, friction SFM allows to distinguish macroscopic domains with different molecular orientations, non-contact mode permits to investigate the crystal without surface deformations as well as longer ranged forces; voltage modulated SFM finally is a new measuring mode employed to deduced the surface polarization.

Surface inspection was initiated using 4-N,N-Dimethylamino-4´-N´-methylstilbazolium Tosylate (DAST) crystals grown as thin plates; the structure consists of layers of two different molecules: anions and cations which are aligned in a herringbone structure. Our SFM measurements on growth surfaces show at first, that they are flat over some 200 nm; surface defects and holes have been observed which most probably stem from the dissolution of the crystal surface due to air humidity. Secondly, we observe on the growing area some triangular structures measuring between 5 and 10 μm in diameter. Measurements on cleaved crystal surfaces increases the vertical resolution to better than 0.01 nm and allow to determine the thickness of individual monomolecular layers. The lateral resolution, however, is limited to ~10 nm due to the weak intermolecular interaction forces. Image contrast in voltage modulated SFM reveals a much higher response signal compared to ferroelectric crystals, elucidating the highly polar character of the DAST sample surface.

References: F. Pan, M.S. Wong, C. Bosshard and P. Günter, *Adv. Mat.* ***7****,(1996) 592.*

Three-Dimensional Reconstruction of Electric Fields at Polar Sample Surfaces by Maxwell Stress Scanning Force Microscopy

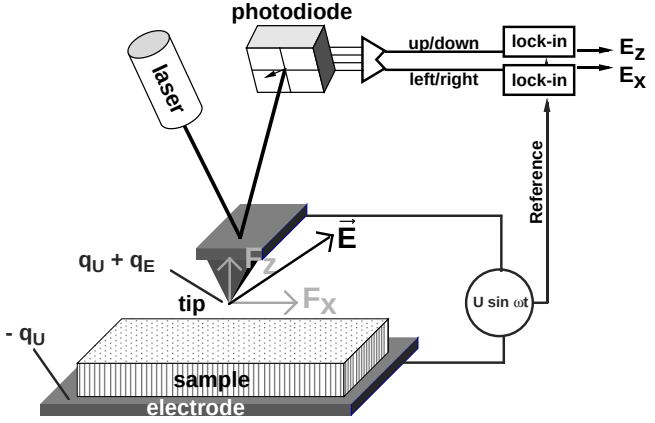
L. Eng and M. Abplanalp

We developed a methode for visualizing the domain structure of ferroelectric crystals by Maxwell stress scanning force microscopy. In this mode of operation an ac voltage is applied between the conductive tip and the bottom electrode of the sample as shown in Figure below. The additional electrostatic force results in minute vibrations of the cantilever. Besides topographic surface features both the amplitude and phase of the induced vibration are monitored and represent the state of polarization of the sample. Therefore the surface dynamics as well as the formation of ferroelectric domains upon phase transition may be investigated.

The four-quadrant photo detector allows to detect both the vibrations of the cantilever perpendicular and parallel to the sample surface (similar to conventional SFM where normal forces and friction forces are recorded). In order to activate tip vibrations the driving frequency ω of the ac voltage applied between tip and bottom electrode has to be larger than the frequency bandwidth of the feed-back loop, but much lower than is the resonance frequency of the cantilever (300 kHz >> ω ≥ 10 kHz).

The applied ac-voltage alternately charges the tip and counter electrode positive and negative. In the presence of an electric field $E=(E_X,E_Y,E_Z)$ the 3-dimensional force acting on the tip is proportional to the product given by $F \propto C \cdot U \cdot E \cdot \cos(\omega t)$.

Demodulating the oscillating force F with high speed digital lock-in amplifiers we are able to record the three components of the electric field vector E_X, E_Y, and E_Z, respectively, which is $F_X \propto E_X$, $F_Y \propto E_Y$ and $F_Z \propto E_Z$.



SFM set-up for recording electric field distributions of polar sample surfaces.

Maxwell Stress Scanning Force Microscopy for Mapping In-Plane and Out-of-Plane Polarization of Ferroelectric Samples

M. Abplanalp and L. Eng

Maxwell stress scanning force microscopy (SMM) was applied to image the electric field distribution of bulk ferroelectric samples. Tri-glycine-sulfate (TGS) polarizes along the *b*-axes, only. Cleaving TGS samples perpendicular to *b* results in polarization vectors pointing either into or out-of the *a*-*c* plane. The electric field above the sample surface will aligne parallel to the internal polarization. Indeed, SMM shows the expected binary contrast for the electric field corresponding to the two polarization states in TGS. The domain wall width of 180° domain walls was measured to approximately 90 nm using SMM which is ~10 times more compared to our earlier experiments performed with non-contact and friction force microscopy. Nevertheless, the sensibility to sample polarization is improved by more than 10 times, and therefore easily balances this drawback.

The ferroelectric domain configuration in Barium-titanate ($BaTiO_3$) is more complex due to the tetragonal unit cell of $BaTiO_3$ at room temperature. Besides polarisation perpendicular to the sample surface, also in-plane polarisation is detectable with the latter having both the polarisation and the corresponding electric field lying parallel to the sample surface. Fig. 1 displays the sample surface topography of $BaTiO_3$ (Fig. 1a, shaded from lower left) together with the two components F_Z (out-of-plane, Fig. 1b) and F_X (in-plane, Fig. 1c) of the electric field, respectively. It is only by Maxwell stress SFM that we are able to record the full 3-dimensional polarisation distribution in such crystals.

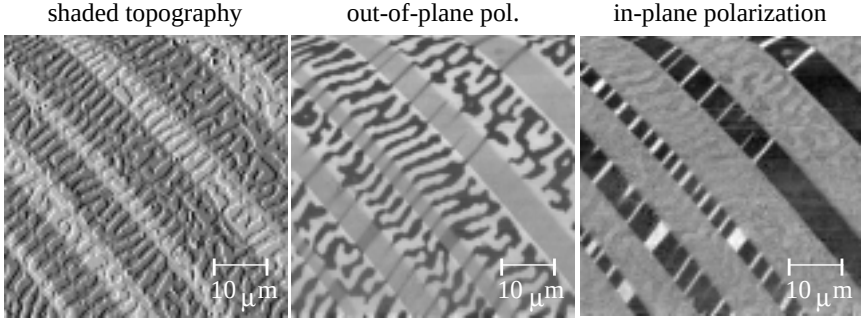


Fig. (a) $BaTiO_3$ sample surface topography, and (b) and (c) the out-of-plane and in-plane component of the electric field at the sample surface, respectively.

Ferroelectric Domain Switching with the Scanning Force Microscope

L. Eng and M. Abplanalp

Direct modification of ferroelectric bulk samples was initiated with scanning force microscopy. Applying a suitable electric field between the conductive tip and the counter electrode results in permanently polarized areas. Such domains may be nucleated either upon phase transitions when cooling the ferroelectric crystals below the critical temperature T_c or by domain switching at any temperature below T_c. The latter experiment strongly depends on the coercive field strength at the particular temperature and the material in use.

Initial experiments were carried out on TGS samples writing square patterns into up- and down pre-polarized regions of the sample. To keep the coercive field low these experiments were performed approximately 2° below T_c. Imaging was achieved using Maxwell stress scanning force microscopy reported in chapter 4.3. Besides such simple structures, also more complex patterns were written like the X-mas star shown in Figure below. Nevertheless, time stability of these domains was too poor for any suitable application (20 min.). Most prominently the asymmetry in the unit cell lattice of TGS favors the lenticular domain shape since this represents the state of minimized electrostatic energy.

Domains written into TGS indeed showed to split into several lenticular domains of a smaller size soon after writing. In $BaTiO_3$, however, all orientations of 180° domain walls are energetically equal due to crystal symmetry. Furthermore, the coercive filed in $BaTiO_3$ measured at room temperature has a value of 100 Volts per mm, only.

As an example the IQE-NLO logo was written into $BaTiO_3$ as presented on the front page of this annual report. While the line width approaches values less than 700 nm, also the time stability is significantly improved (more than 3 days) offering the possibility of the fabrication of physical devices on the nanometer scale.

Direct writing of ferroelectric domains into TGS by scanning force microscopy: the star-shaped pattern has an opposite polarization with respect to the surrounding.
(viewing field 50 x 50 μm^2)

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