

Configurable Nano Patterned Polar Surfaces for Molecular Pattern Formation and Transfer

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We are entering an exciting era that holds the potential for the development of a range of electronic devices that integrate ordered arrays of functional molecules onto nanopatterned surfaces, which present unique applications and truly underpin the development of nanotechnology. Ferroelectrics materials are characterized by a spontaneous, reversible polarization. The presence of a large polarization implies that one can achieve unique surfaces with a controllable combination of surface charge, surface potential, and surface dipole, which can be exploited in patterning and nanoassembly. The fact that the polarization is reversible implies that surface patterns can be written with these features. We have developed and employed scanned probe techniques to create such patterns in ferroelectric surfaces with nanoscale resolution, and we are using these patterns as templates to drive a variety of self assembly processes.

The interdisciplinary team involves Robert Nemanich, Laura Clarke, and Thomas Pearl (Physics), Chris Gorman (Chemistry), and Alexei Gruverman (Materials Science and Engineering). In addition, Angus Kingon (MSE) leads our technology development initiatives, and Maria Oliver-Hoyo (Chem) leads the education and outreach activities.

Central to our understanding of how patterned surfaces can be used as supports and atomically precise templates is resolving how surface properties dictate monolayer growth, crystallinity, and functionality. The first steps towards creating functional nanoscale structures involve grasping how to exploit chemical and physical interactions at the molecular level and determining the degree of correlation between surface properties and single molecule or aggregate interactions. These issues of coherent organization or self-assembly of surface bound molecules impact a broad range of physical phenomena from single molecule device design to heterogeneous catalysis to functional opto-electronic materials. This NIRT supports four interrelated tasks to broadly address these fundamental issues and potential applications.

1. Nanopatterning and Surface Properties

Ferroelectric and other polar materials are utilized in a number of applications (piezoelectric sensors and actuators, pyroelectric sensors and imaging devices, capacitors, etc) representing commercial sales of billions of dollars per year. However, they also display another unique set of characteristics that have not heretofore been exploited or even properly explored. We are

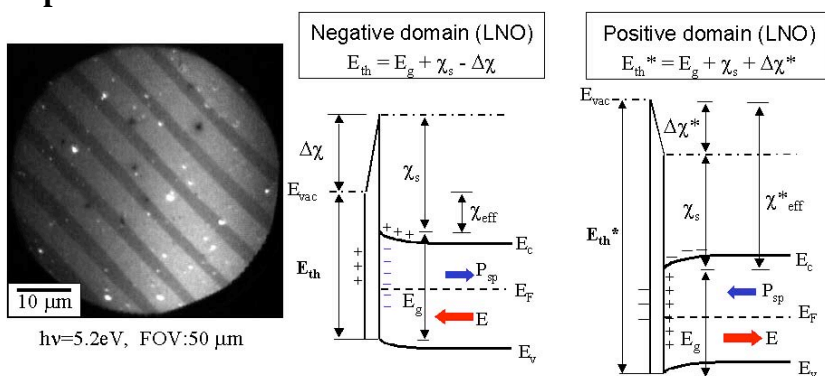


Fig. 1. PEEM image demonstrating polarization-dependent emission and schematics of the charges at the ferroelectric surface of neg. and pos. domains. Note the change in electron affinity.

referring to the unique polar surfaces of these materials which exhibit characteristic surface potentials and surface charges (see Fig. 1.). These properties will enable an exciting and unique set of applications, including local molecular self-assembly, local physical adsorption/desorption, local chemical reactions, local charge transfer reactions, and the manipulation of individual organic molecules. Our goal is to make use of these unique surfaces as configurable and reusable templates for nanoscience and technology.

In order to achieve the necessary control of surface potential and surface charge, we need to understand how the ferroelectric surface develops as a result of the competition between different charge compensation (screening) mechanisms. Photoemission microscopy (PEEM) and scanning probe techniques are being used to explore the effects of the surface dipole that originates between the surface bound charge and the adsorbed charge or surface states. In most current applications of ferroelectrics, the films have electrodes on opposing surfaces, and the polarization charges are screened by compensating charge supplied to the electroded surface. The situation of free polar surfaces is quite different, and the charge compensation mechanisms have not been thoroughly explored, and certainly not controlled. Thus, a significant part of this project is oriented towards developing a fundamental understanding of surface potential and surface charge.

2. The synthesis and use of polar and polarizable, amphiphilic molecules to establish the efficacy of the electrostatic self-assembly paradigm on polarized ferroelectric domains

Although it is now well recognized that self-assembly is going to be an important paradigm for nano-scale fabrication, there are few general assembly strategies. Our goal is to establish that electrostatic interactions between a polarized ferroelectric domain and dipolar, amphiphilic molecules can be a new way to drive self-assembly that is amenable to patterning. We have recently established a procedure to fabricate Ag nanowires on polarity patterned lithium niobate surfaces using a photochemical process. The nanowires which develop at the boundary of the positive and negative domains can be made <100 nm wide and can be 100's of μm long.

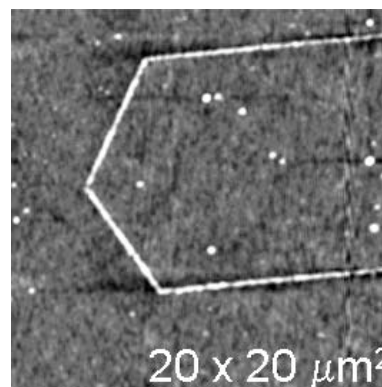


Fig. 2. AFM image of Ag nanowires fabricated on polarity patterned lithium niobate.

3. Local structure of liquid crystal molecules anchored on polarized domains

This research direction is aimed at correlating how polarizable molecules, in particular classes of molecules that comprise liquid crystalline material, interact with a polar surface as it relates to crystallinity and structural phases. For the design of nanoscale opto-electronic devices including chemical sensing surfaces, a detailed understanding of how this surface could serve as a support for these molecules is paramount. The presence of this surface polarization opens the possibility for anchoring and aligning polarizable or ferroelectric molecules like those that exhibit liquid crystalline phases and behavior. For many nanoscale ordered thin films, the crystalline structure of the underlying support directly determines the crystallinity and degree of order in the film. In the case of a localized polar surface, the density of the charge and domain sizes of the patterned film can have a remarkable effect on the behavior of an adsorbed film, the growth mechanisms for ordered structural phases and molecule alignment.

4. Molecular Rotators and Dielectric Response

The dynamics of molecular motion is a fundamental field of study. We are employing a molecular system designed to have predominantly rotary motion, molecular rotors, in conjunction with the well-characterized and controllable ferroelectric surfaces discussed above to achieve two goals: first, to probe the fundamental physics of the interactions between dipolar molecular objects and strong electric fields at nanometer

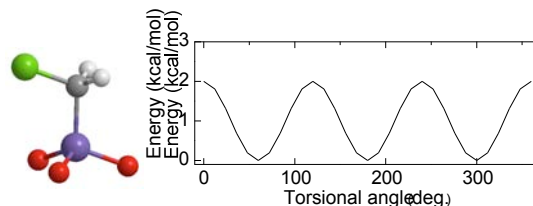


Fig. 3. The chloromethylsilyl rotor with an estimate of its intrinsic torsional potential (1 kcal/mol = 504 K x k_B)

length scales by establishing correlations between the rotor dynamics and the field of single-crystal ferroelectrics; and secondly to work towards utilizing these correlations as a tool to probe and characterize nano-patterned ferroelectric substrates and address the ability to pattern molecular assemblies on such substrates.

Monolayer thin films of rotors have been grown directly onto polarity patterned ferroelectric surfaces between interdigitated electrodes which allow application of the in-plane probe field for dielectric spectroscopy. In the experiments on lithium niobate, a combination of poling and cross-cutting at an angle to the polar axis of the crystal will be used to tune the electric field from the ferroelectric. Hindered molecular rotors are not free to rotate but are constrained to a finite set of orientations defined by their torsional potential and can only reorient due to thermally activated hopping. An example of such a rotor is chloromethylsilyl, as shown in Fig. 3 along with an estimate of its torsional potential in gas phase. Hindered rotors are useful in that, via dielectric spectroscopy, we can obtain quantitative information about torsional barriers, the relative energy of potential minima, and the in-plane dipole, all of which can be influenced by the electrostatic environment of the ferroelectric surface.

Education Outreach

Introductory science courses are ideal scenarios to motivate our students by bringing current research findings into the classroom. Materials can be particularly effective in showing students the connection between microscopic and macroscopic phenomena via tangible applications. Under this NIRT project we are developing new modules that introduce freshman undergraduate students to basic concepts in emerging nanoscience and technology. We are specifically targeting introductory physics and chemistry courses presented in the SCALE-UP approach. The Student-Centered Activities for Large Enrollment Undergraduate Programs, or SCALE-UP, combines lecture and laboratory into one seamless session.

The first SCALE-UP module being developed investigates quantum size effects by examining the absorption and emission spectra of nanoparticles. These types of particles are routinely prepared and are available to us from research studies of the Gorman group. The basic idea that larger particles have red-shifted absorption and emission compared to smaller particles will facilitate discussions of the particle-in-the-box model of quantum mechanics, basic photophysics (a simplified Jablonski diagram), the transition from macroscopic to nanoscopic dimensions, and how the surface of these particles is functionalized to avoid their aggregation (e.g. Ostwald ripening) and to conjugate them within various nano-assemblies (e.g. as biological tags). The students will be presented with nanoparticle samples and asked to make solutions, measure absorption and observe fluorescence using a handheld UV lamp.