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Instrumentation for Enhanced Thin Polymer Film Preparation and Characterization as Photonic Systems

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Abstract:

The instruments purchased or built include: 1. a KSV automated Alternating Layer System, which allows the efficient deposition of alternating Langmuir-Blodgett multilayers from monolayers at the gas-water interface. 2. a KSV spectroscopy trough, which was substantially enhanced to allow laser light scattering spectroscopy at the gas-water interface, observation of morphology at the gas-water interface by Brewster angle microscopy and second harmonic generation measurements of orientation at the gas-water interface. 3. a NanoFilm corporation thin film maker for industrially efficient formation of ultrathin films was built. 4. A Houston Image Force Microscope was purchased and is being used to study the topography and structure of these layers as well as intermolecular forces between the probe and the surface.

J. Adin Mann, Jr. 12/22/2000

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Description of instruments

Monolayers and multilayers are characterized by a number of complimentary techniques. Atomic Force Microscopy (AFM), X-ray diffraction and reflection, and electron diffraction techniques are relatively conventional and do not require a detailed discussion. Similarly, second harmonic generation (SHG) at the gas water interface has been utilized since the late 1980's. However, the use of Brewster angle microscopy (BAM), laser surface light scattering spectroscopy (SLSS), SHG microscopy and during deposition is relatively new and requires a brief discussion. A brief discussion also is included on the new type of probe microscope, image force microscopy we have obtained under this support.

The deposition stations used in the Polymer Microdevices Laboratory (PML) are conventional surface balances that are either automated Lauda troughs, or a KSV alternating trough. We have installed a Brewster Angle Microscope (BAM) using a KSV trough designed for spectroscopy. Also we have installed a surface light scattering spectrometer (SLSS) on the same trough. Moreover, we have combined BAM and SLSS so that it is possible to observe the morphology of the monomolecular film on the same footprint on which SLSS reports monolayer fluctuation spectra. Second Harmonic Generation, SHG, measurements can also be made on the same trough in this same footprint. This combination of techniques allows quantitative measurements of surface visco elastic properties along with morphology as a function of position on the surface.

We have designed and assembled a BAM-SLSS system in which the footprint can be positioned accurately on the surface; we are working toward a scanning system, which will also include SHG. Therefore we can examine the morphology of the monolayer both far from the distortion of the place of deposition (by dipping) and close to the 3-phase contact line between the deposited film, monolayer and substrate; gradients in properties can be measured. Initially, the optical system does require the interface close to the three phase contact line to be flat but fortunately the deposition substrate can be tilted to accommodate this restriction; we expect to be able to work within millimeters of the 3-phase contact line. This procedure is starting to produce a new body of information so as to understand and control the morphology changes that occur in deposition.

In particular BAM-SLSS-SHG will provides information about:

- The morphology of and molecular orientation in the film as distorted by the deposition process including domain structure, surface flow fields and the distortion induced by these flow fields together with:
- Changes in surface viscoelastic moduli and their anisotropy in the deposition region.
-

The next two brief sections comment on the BAM and SLSS methods, each of which is based on optical phenomena. Laser beams are directed onto the surface and either imaged in reflection or the fluctuation correlation of the scattered light is determined. The two footprints can be made to overlap on the surface so that both BAM and SLSS analyze the same patch of surface. For the first time we can see in real time the structures that are reported by SLSS. Presently, data is being collected using overlapping but separate beams for BAM and SLSS. It is possible to do both measurements with the same laser source; the design of such an instrument is being investigated. Subsequent sections outline the SHG, the Houston IFM technique.

Brewster Angle Microscopy (BAM) is a method for using ellipsometry to visualize the structure of monolayers of thickness around 3 nm but microscopic in extent. The method is based on using the fact that the reflectivity of a perfectly flat and homogeneous surface is very near zero for p-polarized light at Brewster's angle. Small deviations away from this condition caused by the monolayer provide a spatial modulation of the reflected light that can be imaged. The method enhances the contrast greatly. For recent results on liquid crystal monolayers of 4'-alkyl [1,1'-biphenyl]-4-carbonitriles (nCB, n=9,10), see the papers of de Mul and Mann and the references therein.

Surface Light Scattering Spectrometer (SLSS). A NASA-Lewis and CWRU team of Mann, Meyer, and Tin developed of a new class of instruments based on optical fiber and diode laser technology. Replacing the large, expensive Argon-ion lasers with very small, battery driven laser diodes has solved many of the problems of conventional designs that made the method difficult. Battery driven detectors are also used along with battery driven amplifiers. Background noise has been greatly reduced. A series of papers explaining this technology appeared in Applied Optics during the Fall of 1997 and in a NATO monograph that also appeared in the Fall of 1997. See references for details. Our group through very careful control of noise sources including the laser noise generated by commercial power supplies has realized considerable refinement of the grating instrument. A second refinement has been the accurate correction for instrument broadening that is due to the finite size of the foot print of the projected grating Also we take into account the frequency response of the band pass filters. The third refinement is the systematic use in data fitting of the full spectrum function for the fluctuations instead of the Lorentzian spectrum function that provides only a center frequency and spectral width frequency. The final refinement involves the realization that channel-channel correlation in the correlogram must be included in weighting the least squares fit, and this was shown to be correct by our group. We have demonstrating that these refinements make possible the determination of the surface response beyond the two viscoelastic coefficients determined in previous work.

Since the spectrometer senses the surface viscoelastic response only in the direction normal to the projected grating lines, a single experiment will not be sufficient to determine the 2-D crystal class. However, experimentally it is very easy to change the direction in which fluctuations are observed when normal incidence is used; the grating that determines the surface direction of q is just rotated. It is therefore possible to determine the anisotropy of the monolayer to small fluctuations. In addition, fluctuations cause the interface to bend slightly; it may be possible to determine bending coefficients of Langmuir films since they appear in the theory with q^4 terms whereas the surface visco-elastic coefficients involve q^2 terms. Indeed, it is possible for us to collect correlation functions over a range of wave numbers.

Thus it is now possible to study the mechanical properties of the monolayer locally (spot size ~ 1 nm) and to scan.

The correlations of these measurements with the deposition process is most interesting especially since we want controlled microprocessing. Note that the surface velocity field caused by the deposition process will split (or broadening at low velocities) the light scattering spectrum (a kind of Doppler effect) but the viscoelastic characteristics will be reported. Indeed, accurate measurements of the velocity field (magnitude and direction) are possible with this non-contact method, again simply by rotating the grating that generates the reference beam.

Houston Method Interface Force Microscopy (IFM). The standard atomic force microscope AFM utilizes a cantilever with the tip attached at one end. The attractive and repulsive forces between the tip and the surface (deposited monolayer or multilayer in our work) are measured. This leads to the tip being accelerated into the surface when the tip gets close enough to the surface and the attractive forces become too great. This means that a large part of the force versus distance profile is unavailable. In addition this type of event increases the chance of creating artifacts on the surface. The Houston system has a similar attachment of the tip at one end of a tiny "bar". However the "bar" is balanced at the center as in a child's teeter-totter. Two pairs of parallel plates, one of each pair is attached above either end of the teeter-totter, can be charged to provide a torque on the teeter-totter and the capacitance measured to determine position of the teeter-totter. The force necessary to keep the bar horizontal is measured, thus allowing the tip/surface force to be measured over the entire range of separation between the tip and the sample. Images can be scanned with force as the set point. Moreover, controlled indentation can be accomplished. Finally, it is easy to dress tips with various LB or self-assembled monolayers so as to probe adhesive (or abhesive) interactions. We now have both IFM and AFM instruments for complementary measurements. The field of probe microscopy is expanding rapidly as new techniques evolve. We are planning to add relevant new techniques over time that will include friction measurements and the local probe of surface potential.

Surface Second Harmonic Generation

The Continuum Surefire Laser-OPO system was installed and used extensively in Prof. Singer's laboratory in order to qualify the laser and experimental setup for use in surface spectroscopy and imaging. The laser was used to study the structure of an absorbed layer of the liquid crystal mesogen pentylcyanobiphenyl (5CB). We observed light-induced alignment of an adsorbed ultrathin film of the nematic liquid crystal, 4,4'-n-pentylcyclobiphenyl (5CB) on a fused quartz surface. Irradiation of the adsorbed layer with polarized ultraviolet light produced homogeneous alignment in a 5CB-filled liquid crystal cell with the axis of easy orientation perpendicular to the polarization direction. The measured anchoring energy increases with illumination, with an observed maximum of 10^{-4} erg/cm^2. Measurements of the phase retardation of polarized light revealed light-induced anisotropy in the irradiated, adsorbed 5CB layer. In addition, pretilt measurements showed near planar alignment of the LC in a cell, while the polarization dependence of second harmonic generation (SHG) suggested a near normal alignment of the first layer. The results suggest that light-induced rearrangement or photo-transformation of 5CB molecules adsorbed on the quartz surface causes the observed phenomenon. The experiment was a demonstration of the construction of such a cell without a separate alignment layer. The results were published in *Physical Review Letters*.

In this experiment, the Continuum Laser system was used to determine the structure of the film using polarized second harmonic generation. We measured the second harmonic intensity in reflection as shown in figure 1 below. The intensity was measured as a function of the azimuthal angle for various settings of the incident and scattered polarization of the fundamental and second harmonic light, respectively. We discovered in these studies that the mesogens were oriented nearly perpendicular to the substrate, probably with the cyano moiety anchored to the surface. The fact that the twist cell possessed planar homogeneous alignment indicates that there is a transition from this near normal alignment to in-plane alignment. We speculate that the aliphitic chain on the non-polar end of the mesogen acts as a "bed of hay" on which subsequent layer reside. We found that the contribution to the signal from the isotropic quartz substrate precluded us from observing azimuthal anistropy of the ultrathin layer. However, we were able to calculate an upper limit on the order parameter of the ultrathin layer and found it to be of a magnitude such that the order parameter of a typical alignment layer likely falls below this.

A number of problems had to be overcome. First, we developed the techniques to subtract the substantial contribution of the substrate to the second harmonic signal. We determined the contribution in a separate experiment where the layer was not included by calculating the effective nonlinear optical susceptibility. This was then subtracted from the sample data. A second major problem was the determination of appropriate wavelength that provided optimum signal to noise. We found in the case of 5CB that resonant measurements were necessary in order to provide a molecular nonlinear optical response large enough to reliably measure above the signal from the substrate. In this case a fundamental wavelength of 532 nm was used. This optimization will need to be carried out for each individual material used in the second harmonic microscope. Lastly, we worked out all of the problems of detection and extraction of the structure of the layer from the data.

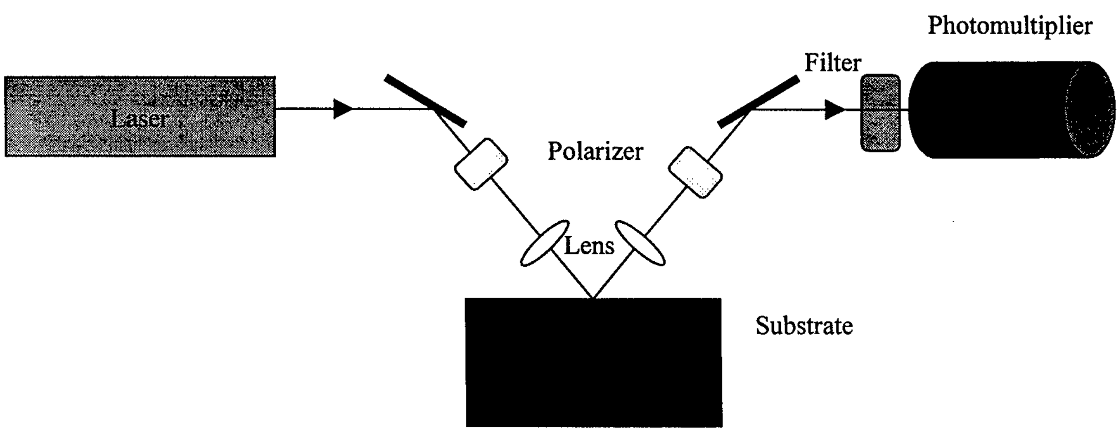

Figure 1. Experimental configuration for surface second harmonic generation.

We have now qualified the structural determination of an amphiphilic surface layer. We have not as yet imaged the second harmonic at the surface, which will await installation in the Polymer Microdevices Laboratory. The basic setup is similar to figure 1 with the substrate replaced by the Langmuir trough, and the photomultiplier replaced with a CCD camera. A setup for transmission in the Langmuir trough is shown in figure 2.

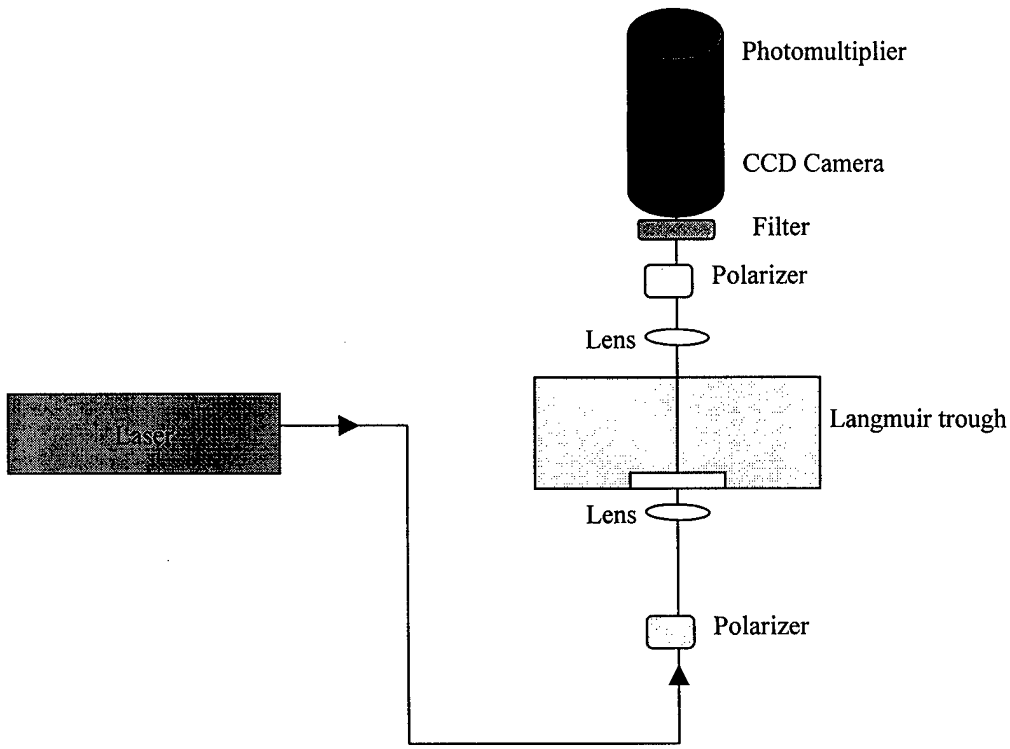

Figure 2. Transmission second harmonic generation microscope.

In addition, the Surelight laser system was used for a funded project to study the nonlinear optical response of multidimensional nonlinear optical chromophores for application in chiral nonlinear optical materials. They have developed a new technique based on hyper-Rayleigh scattering for fully characterizing both the Kleinman symmetric and nonsymmetric rotational invariants of the molecular hyperpolarizability tensor. With this measurement they are able to assess the usefulness of various chromophores for use in chiral materials and have begun to identify molecular structure-property relationships related to chiral nonlinear optical materials. Two publications are in press concerning this work.

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In most cases these papers represent Ph. D. thesis work in the Polymer Microdevices Laboratory.

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