Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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LANGMUIR-BLODGETT FILM WAVEGUIDES

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Abstract The optical characteristics of Langmuir-Blodgett film waveguides is discussed and placed in context in terms of planar waveguide theory. Details of prism coupling measurements are presented with results from specific studies on 22-tricosenoic acid multilayers used as illustrations.

INTRODUCTION

Advances in the development of organic materials has stimulated interest in the use of these materials in planar waveguide systems. With the possibility of strong optical nonlinearities in well aligned structures, techniques for producing such structures need to be developed. One of the potentially most powerful methods is the Langmuir-Blodgett (LB) film technique. This involves the deposition of monolayers of appropriate molecules from mobile monolayers on a fluid (usually water) surface[1]. It is commonly supposed that under suitable deposition conditions it is possible to form highly organised multilayers of organic monolayers with thickness well specified as integer multiples of the monolayer thickness. Typical representation of molecular arrangement in such multilayers is as shown in figure 1. Such an ideal structure is never realised in practice, even if all the molecules are identical (impurities are always present) and the molecules are well aligned there will inevitably be defects present within the films. Of course optical scattering off a low density of defects may not be particularly significant but because of the generally weak bonding between organic molecules the thermal equilibrium population of Schottky defects is likely to be higher than in commonly used inorganics. However there are in general much more severe problems with LB film waveguides simply

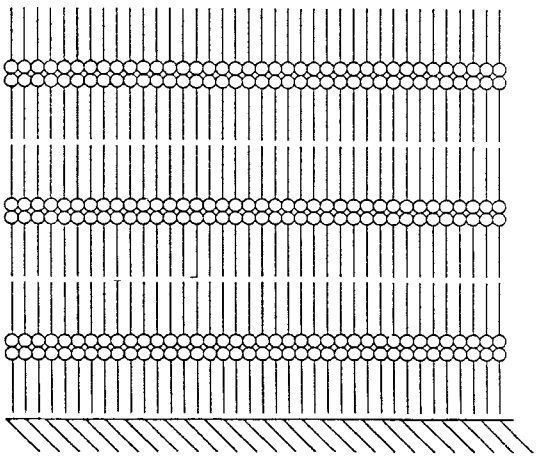

FIGURE 1 An idealised LB film structure

because they rarely approach the idealised structure envisaged above.

Consider even a simple molecule such as one of the alkanoic acids (for example stearic acid) or their salts which are suitably amphiphilic to form a Langmuir monolayer on water and also relatively easy to deposit in multilayer form[2]. If we suppose that there is no significant stearic hindrance caused by the end groups then the long chain aliphatic tails should pack in one of the possible arrangements allowed for infinite aliphatic chains. Kitaigarodskii[3] has shown that there are three dense packing arrangements, orthorhombic, monoclinic and triclinic. If deposited as multilayers it is unclear which of these structures will be the equilibrium form, furthermore there are several different crystal lattices with the same C_2H_4 packing. Peterson and Russell[4] list the 10 structures allowed. Of these 10 only 2 will have the aliphatic chain axes normal to the substrate, one of these has a monoclinic subcell, the other orthorhombic. From these considerations above we find that

a. there are several nearly energetically-equivalent packings of the molecules - this may well lead to mixed crystal phases and a large degree of disorder,

b. even if the molecules do form a single crystal the optical properties of the layer will be complicated since in all cases the crystal will be biaxial and only in the

upright orthorhombic packing will the optical dielectric tensor axes directions be known from crystal symmetry.

Therefore it is unlikely that LB films, unless formed of amorphous (perhaps polymeric) material, will be optically simple. Even if good quality crystals may be deposited it will be only a very few special cases in which pure transverse electric (TE) and pure transverse magnetic (TM) modes will exist. Naive models of molecular arrangements suggested by diagrams such as figure 1 have led in the past to some very simplistic treatments of LB film waveguides and perhaps consequentially overoptimistic views as to their device potential. With this comment in mind we shall now briefly review some of the theoretical background to optical waveguiding in LB films, then move on to examine some of the experimental arrangements and finally discuss specific experiments on 22-tricosenoic acid multilayers.

THEORY OF LAYERED ANISOTROPIC MEDIA

The propagation of guided waves in layered isotropic media is well documented (see eg 5, 6, 7). For anisotropic systems the mathematics becomes somewhat more difficult. Gia Russo and Harris[8] present a treatment of wave propagation in uniaxial media and various extensions to this work exist in the literature (eg 9, 10). However since LB film waveguides are most probably biaxial further extensions to this general case have to be undertaken. For biaxial media with layer geometries for which one imposes no y dependence a 4 × 4 matrix approach is most appropriate. This method was originally developed by Smith[11] and later clarified by Teitler and Henvis[12] and Berremann[13,14]. (A full presentation of this approach for optics of multilayer media using 4 × 4 transfer matrices may be found in Azzam and Bashara[15].) Yamamota et al[16] examined the normal modes of biaxial guides and Ramaswamy[17,18] and Vassell examine special aspects, this later work by Vassell is particularly useful in that it illustrates the solutions of the Eigenvalue problem using the 4 × 4 matrix approach. Because it is a 4 × 4 matrix there are 4 possible Eigenvalues for any homogeneous slab and 4 corresponding Eigenvectors. To find the waveguide modes we simply impose the boundary conditions that in the isotropic bounding media the fields have to decay away from the slab waveguide. For simple systems the TE, TM modes separate into two distinct families. However crystalline LB films should not be expected to support pure modes of this nature since

they are likely to have at best orthorhombic symmetry. Even in this case unless the two optic axes lie in the plane of incidence the modes are not simple TE or TM. It is therefore perhaps somewhat surprising to discover that most experimentalists have treated LB films as uniaxial (or even isotropic) - we shall return to this point later.

Before examining specific situations it is worthwhile briefly reviewing the methods available for experimental study of guided modes in LB films.

EXPERIMENTAL TECHNIQUES

To allow an experimental study of waveguide modes in LB films we have to be able to couple radiation into the film with variable range of momentum along the film. Further this momentum has to be greater than that available for photons travelling in the x direction in either bounding media.

Grating coupling is a commonly used technique for integrated optics (see Tien[7]) but it has received little attention in LB film work. Prism coupling[20] has received

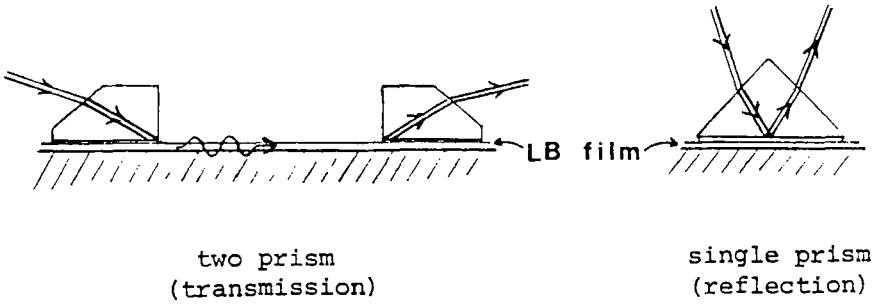

FIGURE 2 Prism coupling arrangements

significant attention for LB and polymeric film work with both single prism[21] and, more usefully as a spectroscopic tool, two-prism[22,23,24] arrangements. These techniques couple radiation into the LB film via either a thin air gap or a coupling medium. Essentially in the single prism technique the attenuated total reflection (ATR) method is used with evanescent coupling to the guided modes (weakly perturbed by the prism). In the two-prism technique

evanescent coupling takes radiation into the film which then propagates along the film and evanescently leaks back out into a second prism.

A variant of the ATR method uses evanescent coupling from the substrate using a low index tunnel barrier[25]. Now the coupling gap is fixed by the thickness of the barrier, deposited before the LB film overlayer. While this does not allow control of the coupling efficiency by changing the gap, it does make studies in the visible region of the spectrum (air gap ∿500 nm) much easier.

EXPERIMENTAL RESULTS

Pitt and Walpita[26,27,21] report optical waveguiding in LB films of cadmium stearate and N-(n-Octadecyl)-acylamide. They analysed their data in terms of a uniaxial slab with its optic axis perpendicular to the substrate. This leads to different apparent film thicknesses for TE and TM modes, for example in their table III[21] they give monolayer lengths of 2.28 nm and 2.53 nm deduced from the extraordinary and the ordinary mode data respectively. Clearly, since they suggest that the monolayer thickness is precise to a fraction of an Angstrom, this discrepancy in thickness implies a misinterpretation of their data - perhaps the assumption of a uniaxial axis normal to the substrate was erroneous. Barnes and Sambles[25] studied multilayers of 22-tricosenoic acid using the prism geometry illustrated in figure 3.

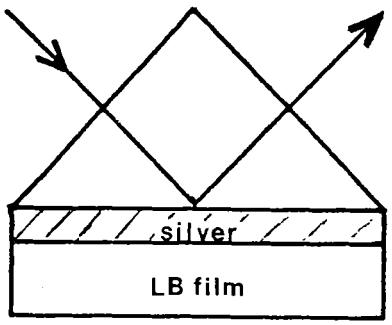

FIGURE 3 Prism arrangement for studying LB films

By fitting the angular dependent reflectivity to Fresnel theory for their system, having first obtained the silver parameters by fitting the surface plasmon-polariton resonance data, Barnes and Sambles[25] were able to obtain an accurate thickness and two optical dielectric constants.

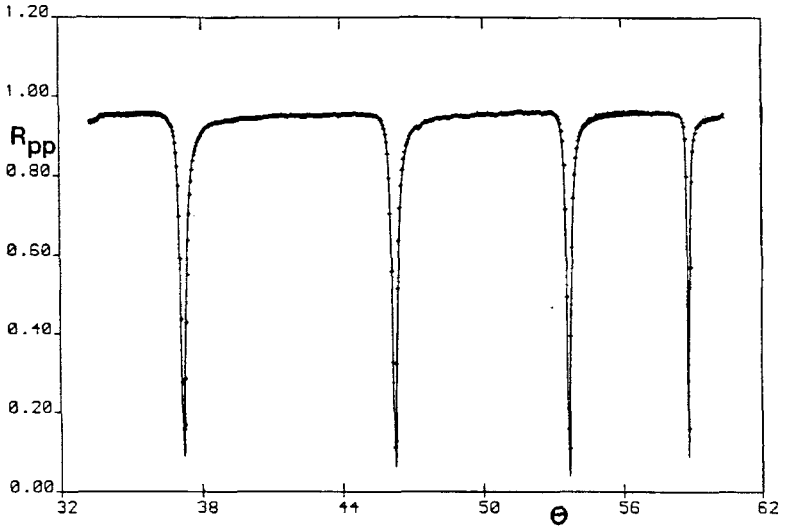

FIGURE 4 Fit of theory to reflectivity data

In these experiments the propagation direction was parallel to the dipping direction. If we examine the LB film deposition procedures it is clear that orthorhombic or monoclinic with one right angle axes pair in the plane of the substrate can satisfy the symmetry imposed by the normal perpendicular dipping technique. If the energetics favours neither of these structures then unless the symmetry is deliberately broken to tilt the lattice axes to one or other side of the dipping axis a mixture of crystallites, with overall symmetry about the xz plane is likely to occur. Thus it is likely that for most LB films pure TE and TM modes will occur for propagation along the dipping direction. Of course a corollary of this is that

for many structures this will be an 'effective' medium, being the average response of at least 2 orientations of triclinic crystallites imposed by the dipping symmetry. This leads to strong optical scattering and poor wave-guiding. In an experiment designed to show that the 22-tricosenoic acid was indeed biaxial, Barnes and Sambles[28] deposited waveguides onto high refractive index glass pyramids with the geometry shown in figure 5.

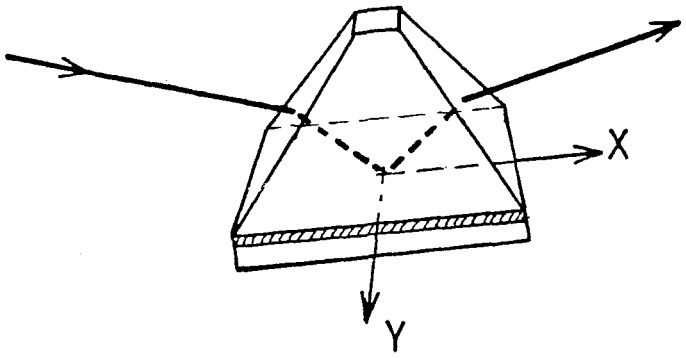

FIGURE 5 Pyramid geometry for studying LB films

Now modes could be excited for propagation along the X axis (the dipping direction) and the Y axis (perpendicular to the dipping direction). Data of reflectivity against angle in the second case shows that the system is not arranged with a single optic axis normal to the substrate. All the resonances were of mixed character, using p-polarised (TM) incident light some s-polarised (TE) light was reradiated for the angles of resonance, figure 6 illustrates this. To fit this data to theory requires a full biaxial model of the system following Berreman's[13,14] approach. The data for X propagation (TE and TM) is first fitted to give the film thickness, ε_Y and a combination of the other two tensorial ε values (those lying in the xz plane). Data for Y propagation is then fitted using the known film thickness and changing the tilt of the tensor axes in the xz plane until a fit is obtained (adjusting the two ε values to maintain the combined parameter needed for the TM modes for X propagation). From this procedure

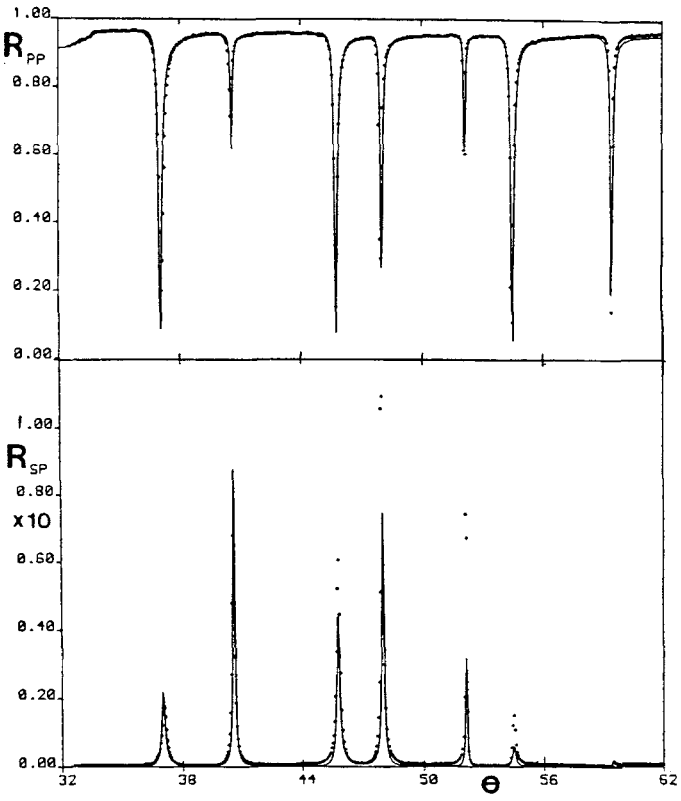

FIGURE 6 Reflectivity data for mixed modes

a full characterisation of the optical tensor is completed. These experiments were then repeated for a range of surface pressures and it was found that the film thickness and molecular tilt varied with surface pressure[29]. This is not possible if a unique crystal structure with basal plane parallel to the substrate - the ideal LB structure - is formed. By varying the LB film thickness and the radiation wavelength further information on bulk optical scatter and surface roughness of the LB films was obtained[30]. Thus these relatively simple optical experiments together with careful comparison between theory and data have significantly extended our understanding of the structure of this particular LB film material. They imply that in general fabrication techniques for making good quality single crystal LB films need to be developed before these novel range of materials can be used to their full potential as optical waveguides.

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