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A Device for Surface Study of Confined Micron Thin Films in a Total Internal Reflection Geometry

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A device for surface study of confined micron thin films in a total internal reflection geometry

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A device to probe the molecular structure of materials next to a solid interface in a thin film geometry has been developed. The device can produce controlled thicknesses as small as 1 μm with parallelity better than 0.003°. We have shown that the thickness and the parallelity of the film produced between two optical surfaces can be quantified using white light and monochromatic light interferometry, respectively. In addition, this apparatus allows the study of these films in a static state or under shear using spectroscopic techniques involving transmission or reflection measurements. [DOI: 10.1063/1.1473222]

INTRODUCTION

Recent studies show that infrared-visible sum frequency generation spectroscopy (SFG) can be used to probe hidden interfaces with total internal reflection geometry.[1] Using SFG to probe the structure of organic molecules at the solid hidden interface in a condition of flow or pressure would help answer fundamental questions associated with stick–slip response, lubrication, adhesion, and surface chemistry.[2,3] In order to use SFG to perform these measurements in total internal reflection geometry, it is necessary to devise an apparatus that can bring two macroscopic surfaces, one consisting of a prism and one of a flat plate, to a controlled and parallel separation. Though similar parallel plate instruments have been developed to perform optical,[4] neutron,[5] and x-ray measurements,[6,7] none allows the use of optical total internal reflection to characterize the surface of the confined film. Also, the surface force apparatus used to study confined fluids requires a crossed cylinder geometry and has a typical contact area of <100 μm,[8] making it difficult to probe surfaces using optical techniques. Because of the inherent surface sensitivity of SFG, the apparatus developed in this article allows the study of the surface of a confined film in a static or dynamic state, whereas neutron or x-ray measurements can only be used to characterize the bulk of the film using similar apparatuses.[5–7]

There were two main challenges to overcome for the successful development of the experimental apparatus. The first challenge was to devise a protocol to measure the separation and parallelity of two surfaces, one consisting of a prism and the other a flat plate. The second challenge was to avoid using metallic coatings, as used in Refs. 4 and 7, on the prism surface since nonresonant SFG signals from metal surfaces may be orders of magnitude higher than the resonance signals from organic molecules. In the first section of the paper, we describe the theoretical model used to determine separation and parallelity of the surfaces based on interferometry techniques in the presence or absence of metal coatings. In the second section, we describe the construction of the device and the procedure to measure separation and tilt between the two surfaces.

INTERFEROMETRY MODEL

The basic theory of wave propagation in stratified media has been described in Ref. 9. Consider a plane, time-harmonic electromagnetic wave propagating through a multilayered medium. Any arbitrarily polarized plane wave can be resolved into two waves: one polarized in the plane of the surface and one polarized perpendicular to the surface. The boundary conditions at a discontinuous interface for the two polarization components are independent of each other. Therefore, the two waves will also be independent. Solutions to Maxwell equations can conveniently be expressed in terms of matrices as seen in Eq. (1):

$$Q_0 = MQ, \tag{1}$$

where M is characteristic matrix of a stratified medium and Q_0 and Q are defined by Eq. (2)

$$Q_0 = \begin{bmatrix} U_0 \\ V_0 \end{bmatrix}$$

and

$$Q = \begin{bmatrix} U(z) \\ V(z) \end{bmatrix}. \tag{2}$$

Consider a single dielectric film that extends from $z=0$ to $z=z_1$ and that is bounded on each side by a homogeneous, semi-infinite medium. A, R, and T denote the amplitudes of the electric vectors of the incident, reflected, and transmitted waves. Let ϵ_0 and ϵ_2 be the dielectric constant of the first and the last medium and let θ_0 and θ_2 be the angles that the incident and the transmitted waves make with z direction. In this case, the four quantities U_0, V_0, U, and V are connected by the relations

$$\left.\begin{aligned} U_0 &= A + R, & U(z_1) &= T, \\ V_0 &= p_0(A - R), & V(z_1) &= p_2 T, \end{aligned}\right\}, \tag{3}$$

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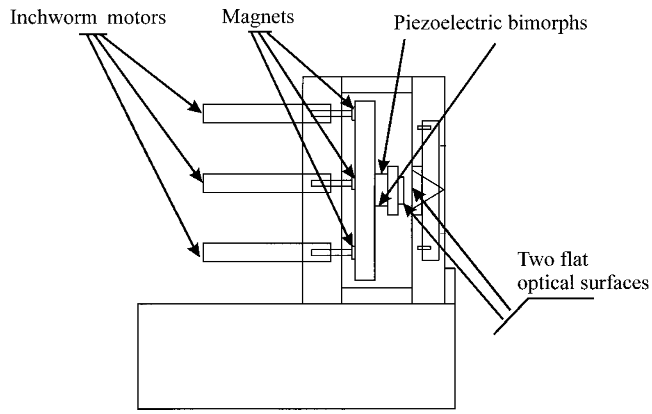

FIG. 1. Schematic diagram of the parallel plate apparatus.

where p_0 and p_2 are given by the following equations:

$$p_0 = \sqrt{\epsilon_0}\cos(\theta_0), \quad p_2 = \sqrt{\epsilon_2}\cos(\theta_2). \tag{4}$$

The reflection and transmission coefficients of the film are as follows:

$$r = \frac{R}{A}, \quad t = \frac{T}{A}. \tag{5}$$

In terms of r and t, the reflectivity and transmittivity are described by Eq. (6)

$$\mathbf{R} = |r|^2, \quad \mathbf{T} = \frac{p_2}{p_0}|t|^2. \tag{6}$$

The same treatment can be extended to a layer of N thin homogeneous films with interfaces lying at $z = 0,\ z_1, z_2, \ldots, z_N$, with $0 \leqslant z \leqslant z_1, \ldots, z_{N-1} \leqslant z \leqslant z_N$. Equation (1) can then be generalized by Eq. (7)

$$Q_0 = M(z_N)Q(z_N),$$

where

$$M(z_N) = M_1(z_1)M_2(z_2 - z_1), \ldots, M_N(z_N - z_{N-1}). \tag{7}$$

With the help of Eq. (7), transmission and reflection from any multilayered medium can be derived.

EXPERIMENTAL SETUP AND RESULTS

The basic setup of our experiments is shown in Fig. 1. To provide parallel alignment and fine control of separation between two surfaces, three tripod legs of inchworm motors were used. The inchworm motors, Burleigh IW-700's have a travel distance of 50 mm and a step resolution of 4 nm with a Burleigh 6000URL controller. A plate was fixed to the inchworm motors using magnets. Attached to the plate by means of piezoelectric bimorphs is an optically flat window. The bimorphs provide the capability of performing shear measurements.[4] To complete the thin film geometry, our apparatus can hold another optical window or a prism giving the flexibility to perform spectroscopic measurements in transmission through two windows, or in internal reflection using the prism.

To illustrate that parallel alignment is possible using this apparatus, an interferometric method was applied. With two optical surfaces in place, we can assume that our device creates a homogeneous dielectric film situated between two homogeneous media as shown in Fig. 2(a). When a structure of this nature is illuminated by a point source of quasimonochromatic light, an interferometric pattern of concentric circles should appear if the optical surfaces are parallel. An image of these fringes created when two silver coated BK7 optical windows, separated by an air gap, were illuminated by a sodium lamp (Oriel Instruments) is shown in Fig. 3(a). Silver films were used because the contrast of the fringes is enhanced when one or both of the optical surfaces are coated with a partially reflective metallic film. If the two optical surfaces are off parallel, the interferometric pattern changes from concentric circles to parallel lines. The alternating bands of light and dark appear because certain distances between the tilted plates satisfy the condition for destructive interference, which occurs when the spacing is $d = m\lambda/2$; $m = 1,2,3\ldots$. To estimate an upper bound of tilt angle, we assume that there is at most one dark band in our image $(m = 1)$. This means the distance between the plates at the extreme edges of the viewing area can differ by at most 295 nm when using a sodium lamp. With a viewing area of 5 mm, the tilt angle between the surfaces is at most 0.003°.

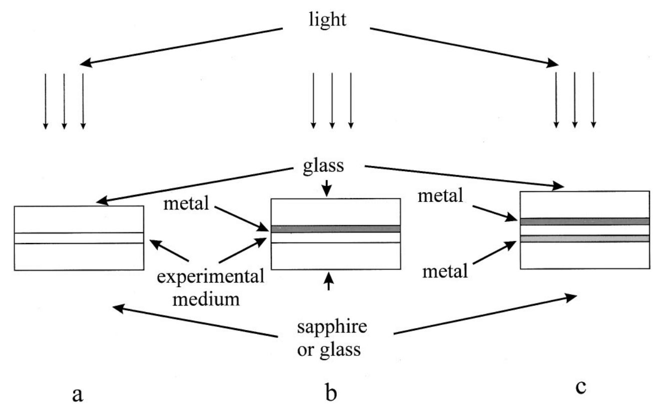

FIG. 2. (a) Three-layer model composed of both optical surfaces and the medium to be studied between them. (b) Four-layer model with one of the optical surfaces coated with a partially reflective metallic film. (c) Five-layer model with both optical surfaces coated with partially reflective metallic films.

To estimate the tilt between the two surfaces with a higher resolution, it is possible to measure the finesse F_d of the system. Let us assume that the finesse F_d depends on the

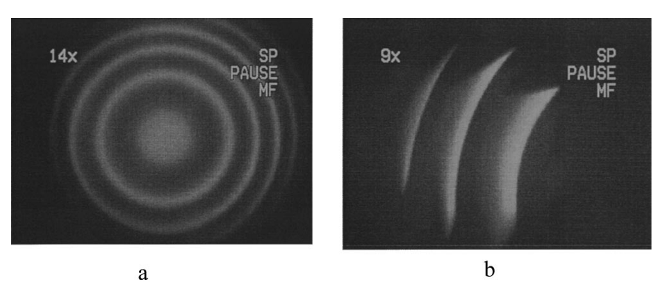

FIG. 3. Interference fringes produced when monochromatic light from a sodium lamp is transmitted through: (a) a five-layer system of two BK7 optical windows coated with silver films 17 and 30 nm thick and air between the surfaces. This system was adjusted for optimum parallelity. (b) A four-layer system of one silver coated BK7 optical window and a sapphire prism.

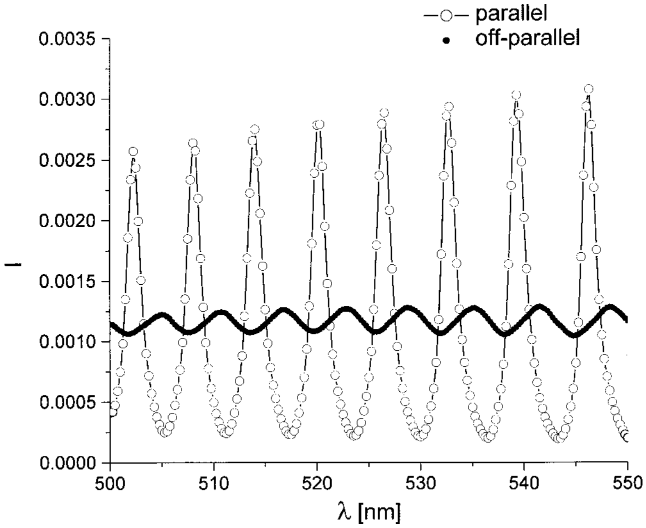

FIG. 4. White light interference spectra produced from two silver coated (17 and 36 nm thick) BK7 optical windows with an air gap adjusted for parallelity (open circles) and with surfaces off parallel (solid circles).

magnitude of the departure from plane parallelism. For the particular case where the defect is a slight spherical curvature of the plates such that nd changes by λ/q between the center and the edge of the plate, $F_d = q/2$.[9] Practically, there are several factors that define the total finesse of the system, but only two are important: First, the reflectivity of the plates R defining the reflectivity finesse $F_r = \pi\sqrt{R}/(1-R)$. The calculated reflectivity of the silver coated (36 nm thick) window for a sodium light source is about 0.85, making, $F_r \approx 19$. Second, the loss of light between the plates due to the nonperfect quality of the surfaces, defined by the flatness finesse $[F_t = \text{flatness of plate}/(\lambda\sqrt{2})]$. In our case the flatness of the plate is λ/5 so the flatness finesse is 3.54. The total finesse of the system is given by $F_T = (F_r^{-2} + F_t^{-2})^{-1/2}$ and is about 3.48.[10] If we apply the total finesse F_T to the finesse for the nonparallel plates F_d, we see that it is possible to obtain off-parallility of as little as $d \approx 85$ nm, which corresponds to the tilt angle between surfaces of about 0.002°.

To determine the separation between the optical surfaces, we have used white light interferometry. In white light interferometry, the spectral features of an interference pattern (peaks and valleys) should appear at certain wavelengths depending on the separation. In our system, white light from a Fiber Lite PL 800 (Dolan Jenner) was chopped (light chopper model 196, Princeton Applied Research, at 400 Hz) and directed through two BK7 windows (Melles-Griot, λ/5) or one window and face of a sapphire prism. The light was then collected by a lens (focal length of 15 cm) and dispersed by a spectrometer (SP-500, Acton Research). The signal was detected by a photodiode (model 818 SL, Newport), amplified by a SR850 lock-in amplifier (Stanford Research) and a computer recorded the light intensity. The transmission spectra were compared to the theoretical spectra obtained from Eqs. (1)–(7). The optical properties of silver were taken from Ref. 11. In the first example, the transmission spectra from two silver coated BK7 surfaces [as in Fig. 2(c)] are shown in Figs. 4 and 5(a). Also shown in Fig. 5(a) is the theoretical transmission spectrum calculated using a five-layer model.

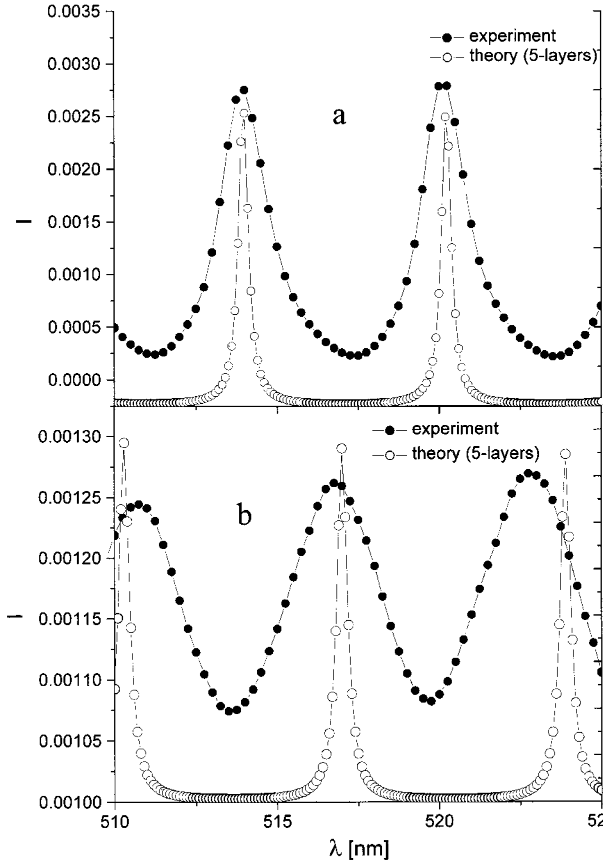

FIG. 5. (a) White light interference spectrum produced from two silver coated (17 and 36 nm thick) BK7 optical windows with an air gap between (solid circles). A theoretical spectrum is also shown calculated using a five-layer model and an interplate spacing of 14.66 μm (open circles). (b) White light interference spectrum produced from an identical system with a tilt produced by translating one of the inchworm motors ~2 μm (solid circles). The theoretical spectrum was produced assuming parallel plates with a spacing of 13.50 μm (open circles).

Translating, one of the inchworm motors roughly 2 μm produces a significant tilt as well as a significant change in the transmission spectrum as seen in Fig. 4. Notice that the peaks from the off-parallel system are broader and shorter than for the parallel system in Fig. 4.

The contrast or visibility ν of the interference pattern produced by two quasimonochromatic beams with degree of coherence γ_{12} is defined by Eq. (8).

$$\nu = \frac{I_{\max} - I_{\min}}{I_{\max} + I_{\min}} = 2\,\frac{\sqrt{I_1}\sqrt{I_2}}{I_1 + I_2}\,\gamma_{12}, \tag{8}$$

where here $I_{\max}$ and $I_{\min}$ are the maximum and minimum intensity of the fringes, respectively. I_1 and I_2 are the intensity of any two interfering light beams (see, for example Ref. 9, p. 569). The simplest way to think of our interferometric system is to imagine there are two sources of light. The degree of coherence between these two sources can be assigned by the tilt angle and the spectral resolution of the optical system, and we expect a decrease of the visibility with increasing tilt. This effect is seen when we look at the experimental curves in Figs. 4 and 5. The broadness of the experimental spectra relative to the theoretical fits in Fig. 5 is due to the finite spectral slit of the system. In our experi-

TABLE I. Theoretical visibilites for various experimental systems.

Number of layers	Visibility (γ_{12}), $N_{\mathrm{media}}=1$	Visibility (γ_{12}), $N_{\mathrm{media}}=1.45$
3	0.114	0.005
4	0.562	0.241
5	0.993	0.988

ments the entrance and exit slit widths of the spectrometer were both 250 μm, and for the spectral range of 500–700 nm, this corresponds to a spectral resolution of ~0.50 nm.

We can apply the same principles we have discussed so far to achieve parallel alignment between an optical window and a sapphire prism. A monochromatic interferometric pattern of concentric circles, similar to the one obtained for BK7 optical windows, can be seen in Fig. 3(b). We only observe half of the image because only half of the image escapes through each face of the prism. White light was directed through a window (BK7, Melles-Griot, λ/5) and collected through one face of a sapphire prism. First, we compare the theoretical value of the visibility for systems with three (without metallic films), four (one metallic film), and five layers (with metallic films) [Figs. 2(a), 2(b), and 2(c)] and with different refractive index of the confined film. Table I summarizes the data. As we can see from Table I, the visibility for the four- and five-layer systems does not change drastically with refractive index of the studied medium, while in the three-layer system, the visibility decreases by a factor of 20. This means that separations can practically be measured using white light interferometry if only one surface is coated by silver or another reflective metal. Figure 6 shows experimental and calculated transmission spectra for a four-layer system with a silver coated BK7 optical window and a sapphire prism.

The principal limitations on the minimum plate separation are airborne dust, the capability of white light interferometry, temperature instability, and surface roughness. The dust particles and temperature instability are a problem at present because the apparatus is stored in an ordinary laboratory environment. Dust limits plate separations to not less than ~4 μm. In the absence of dust, thermal expansion limits the plate separation. We have observed a separation change from 17.34 to 18.06 μm while the temperature changed 2 °C. This is what we expect for the thermal expansion of aluminum ($\alpha=22.4\times10^{-6}$ K^{-1}) with linear dimensions of ~1 cm. In the spectral range of 400–700 nm, we should be able to determine interplate spacings with an error of only 0.1 μm with thicknesses as small as 1 μm assuming stable experimental conditions.

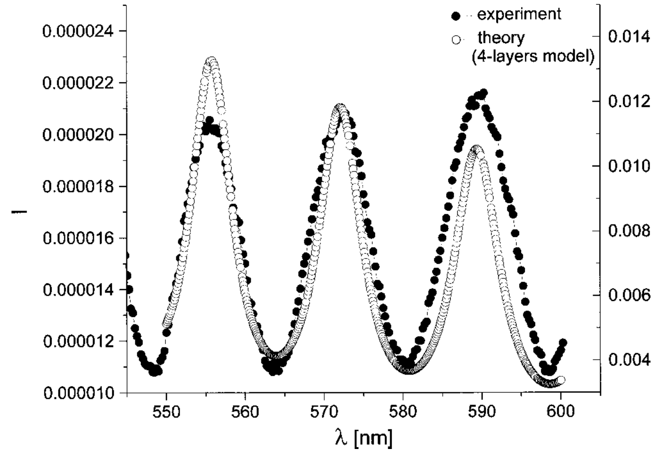

FIG. 6. White light interference spectrum produced by a four-layer system composed of one silver coated (42 nm thickness) and one sapphire prism with an air gap in between (solid circles). The theoretical spectrum was calculated using the same optical parameters as in Fig. 4 and a plate separation of 9.70 μm (open circles).

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