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ORGANIC AND POLYMER CRYSTALLINE FILMS FOR SPATIAL LIGHT MODULATION

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Final Report



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Air Force Systems Command
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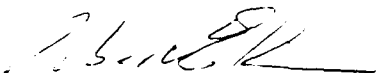
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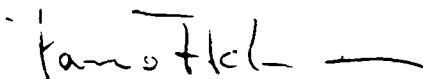
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| 19. ABSTRACT (Continue on reverse if necessary and identify by block number) In this report, the work done during the last phase of this program is described. The efforts involved two components of the program in polymeric ultrathin films, second harmonic generation measurements to characterize the second order nonlinearities, and capacitance measurements of deposition quality and water entrapment during deposition. With regard to second harmonic generation, the components of $\chi^{(2)}$ and the molecular orientation in Langmuir/Blodgett films of hemicyanine dye on glass substrates are reported. Decay of the signal because of molecular rearrangement and diffusion of impurities is discussed. For the capacitance sensor, subphase (water) entrainment is described as a function of deposition speed and of material composition. | | | | |
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INTRODUCTION

This report covers the period 1 October 1985 to 8 December 1986. In this report, the performance obtained through Langmuir/Blodgett (L/B) deposition on multimonomolecular thin film systems is discussed.

The possibility of developing a useful electro-optic or all optical device made from organic materials hinges on the ability to organize these molecules into favorable geometries such that their inherently high hyperpolarizabilities can be realized in macroscopic structures (Ref. 1). The highly polarizable cyanine dyes are candidates for use in such devices while the Langmuir/Blodgett deposition technique has the capability to provide control over the process of organizing these molecules into useful structures.

SECOND HARMONIC GENERATION (SHG)

The technique of surface SHG (Ref. 2 and 3) is used to measure the component's $\chi^{(2)}$ surface and the molecular polar angle (angle the molecular axis makes with the surface normal). The experimental setup is described in Ref. 4. The observed signals from the dye films were calibrated against an x-cut quartz crystal ($\chi_{xxx} = 3.64 \times 10^{-13} \text{ m}^2/\text{V}$). The dye films showed no signal dependence upon rotation about the surface normal. This symmetry property implies that only χ_{xyz} , χ_{xxz} , $\chi_{zxx} = \chi_{zyy}$, and χ_{zzz} are nonzero. χ_{xyz} was nearly two orders of magnitude smaller than χ_{zzz} , χ_{xxz} , and χ_{zxx} in single and multiple layer films with $\chi_{zzz} \sim 3 \times 10^{-19} \text{ m}^2/\text{V}$ and $\chi_{zxx} \sim \chi_{xxz} \sim 4 \times 10^{-20} \text{ m}^2/\text{V}$. By assuming that the molecular hyperpolarizability is dominated by one component β_{zzz} (z-axis along molecular axis), and using the following relationships,

$$\chi_{zzz}^{(2)} = N_s \langle \cos^3 \theta \rangle \beta_{zzz}$$

$$\chi_{zxx}^{(2)} = \chi_{xxz}^{(2)} = \frac{1}{2} N_s \langle \cos \theta \sin^2 \theta \rangle \beta_{zzz}$$

the average polar angle was calculated to be $\theta \sim 30^\circ$, where the molecular surface density, $N_s = 3.33 \times 10^{18} \text{ molecules/m}^2$. Multiple layer z-type films have

shown enhanced SHG (Ref. 4). Films have been grown that continue to show a better than linear enhancement up through 22 layers (Fig. 1). In fact, the 22-layer sample, which is about 660 Å thick provides an SHG signal that is only two orders of magnitude smaller than the quartz reference. This corresponds to a χ_{zzz} for the film $\sim 2 \times 10^{-18} \text{ m}^2/\text{V}$. The average polar angle remains ~ 30 deg for these multilayer films suggesting that each layer retains the same structure as a monolayer.

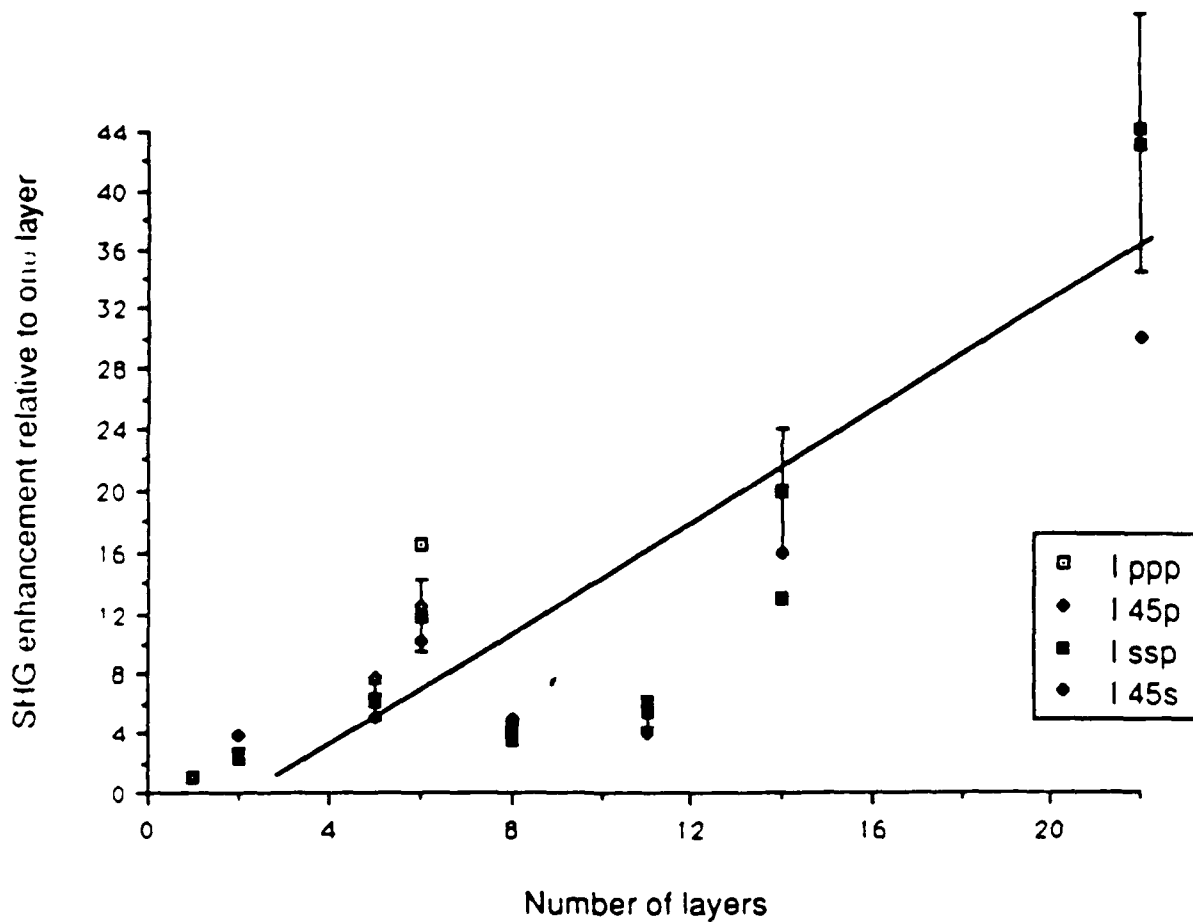


Figure 1. Multilayer enhancement of the SHG in Langmuir/Blodgett films of hemicyanine dye.

While these films seem to be unharmed by the laser irradiation, the SHG signal decays with time (Fig. 2). Molecular reorientation seems to account for only a small part of the decay as evidenced by a slight shift (~ 5 deg increase) in the average polar angle during the decay time (Fig. 3). Multiple layer films were found to decay slower than do monolayers, and so the postulate is that the remainder of the decay is due to diffusion of impurities from the air into the film causing a more symmetric electron distribution around the chromophores and, hence, diminishing the nonlinear polarization. More experiments will be necessary to completely understand the mechanism of the decay.

To attack the problems of stability and robustness a variety of experiments was performed with polymeric mixtures consisting of poly (octadecylmethacrylate), PODMA, and hemicyanine to see if reorientation (that occurs with time) can be prevented by encasing the dye in a polymer matrix to enhance the alignment of the dye (PODMA is known to have side chains which orient nearly perpendicular to the surface). Also, chemically attaching the dye to the PODMA was attempted to enhance the material properties.

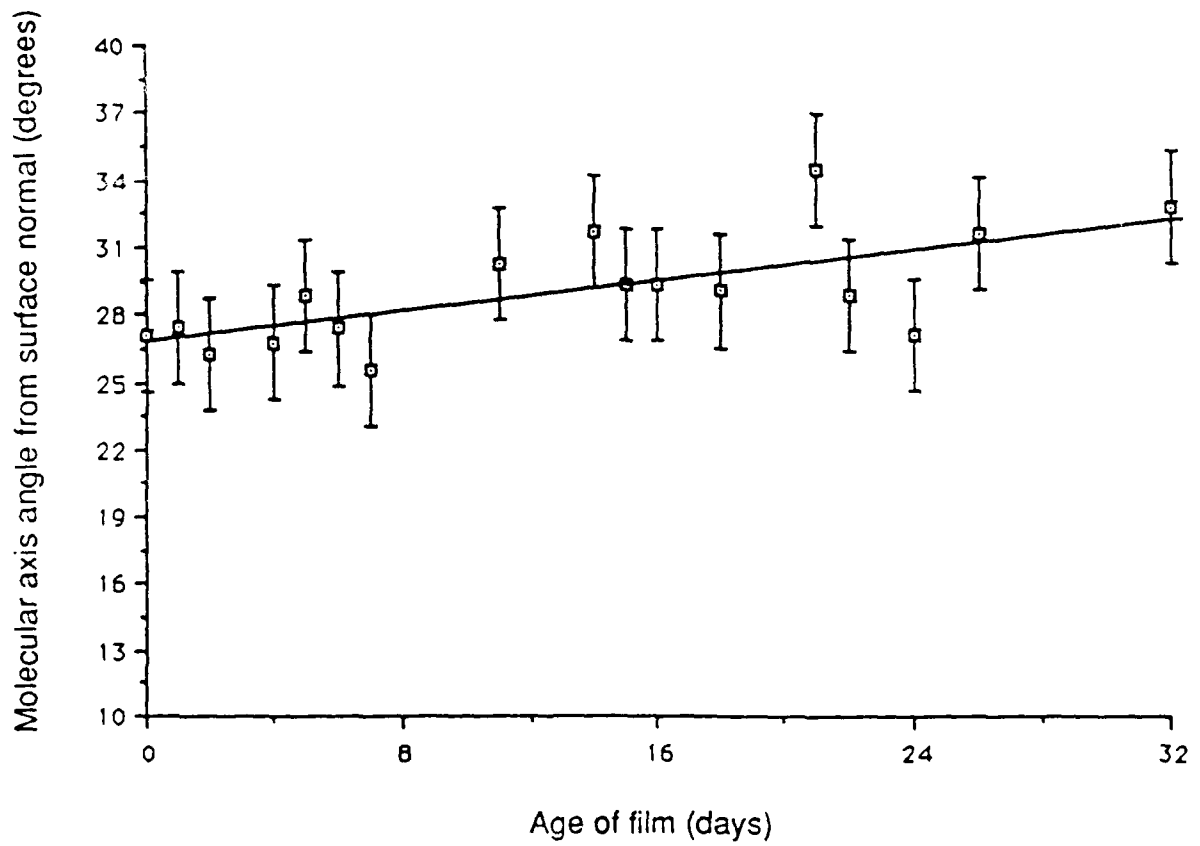


Figure 3. Increase of polar angle as the film ages.

CAPACITANCE SENSOR

An on-line capacitance sensor was used to study subphase entrainment during Langmuir/Blodgett deposition of n-docosyl merocyanine, n-docosyl hemicyanine (with 0.01 M NaClO_4 in the subphase), and cadmium arachidate (with 0.005 M CdCl_2 in the subphase); the monolayers were deposited at surface pressures of 24 mN/m, 25 mN/m and 20 mN/m, respectively. The sensor (Fig. 4) was an interleaved comb pattern that was etched microlithographically from an aluminum-coated glass slide. The fingers were on the average 18 μm wide, 18 μm apart, and about 0.5 μm thick. The approximate length of each finger was 6 mm. The sensor was connected to a GenRad RLC Digibridge capacitance meter capable of measuring down to 0.01 pF. The meter was interfaced to an IBM AT Personal Computer; the data acquisition system was capable of sampling at a frequency of 12 points per second.

During subphase withdrawal the capacitance of the sensor decreased as water was progressively displaced by an air/monolayer dielectric. The monolayer contribution to the capacitance was of the order of 0.05 pF against a background capacitance (Ref. 5) in air of about 60 pF. The background capacitance when the sensor was completely immersed in the subphase was above 500 pF; the large relative dielectric constant for water (≈ 78) enables any entrained subphase to be detected during monolayer deposition. When entrainment occurred, the capacitance exceeded the background capacitance in air, at the time the lowest finger of the sensor passed through the interface (location C shown in the inset of Fig. 5).

Experiments in which the sensor was dipped through a clean interface (no monolayer present) showed no entrainment of water when the dipping speed was < 0.37 mm/s. (A typical capacitance versus time trace is shown as curve 1 in Fig. 5.) At higher dipping speeds some entrainment occurred, presumably because of water being trapped between the fingers. When cadmium arachidate was deposited, entrainment was detected on the first upstroke only. Subsequent depositions showed no evidence of entrainment even up to the highest dipping speed used (1 mm/s). The capacitance trace (2) in Fig. 5 is typical for the arachidate deposition.

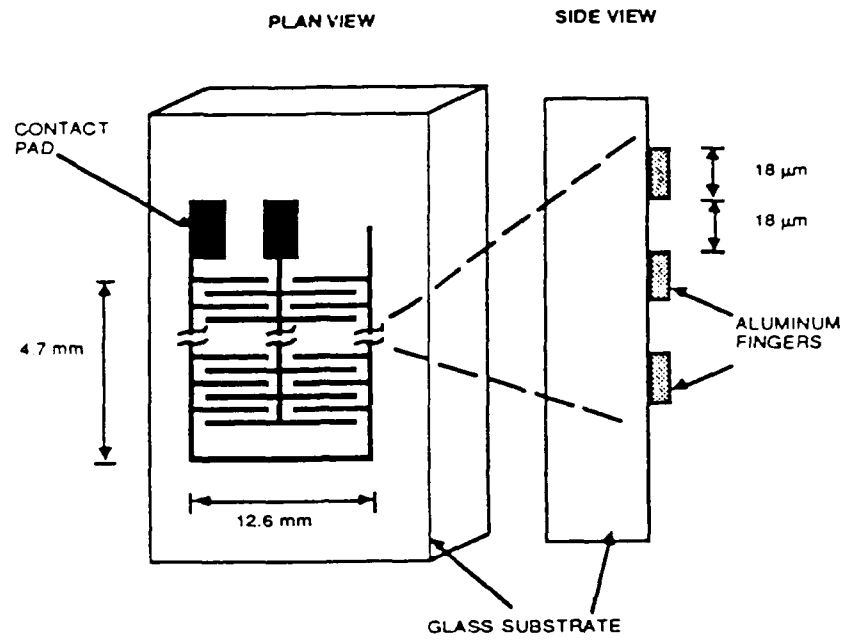


Figure 4. Schematic of the capacitance sensor etched on a glass substrate. The height of the aluminum fingers is about 0.5 μm.

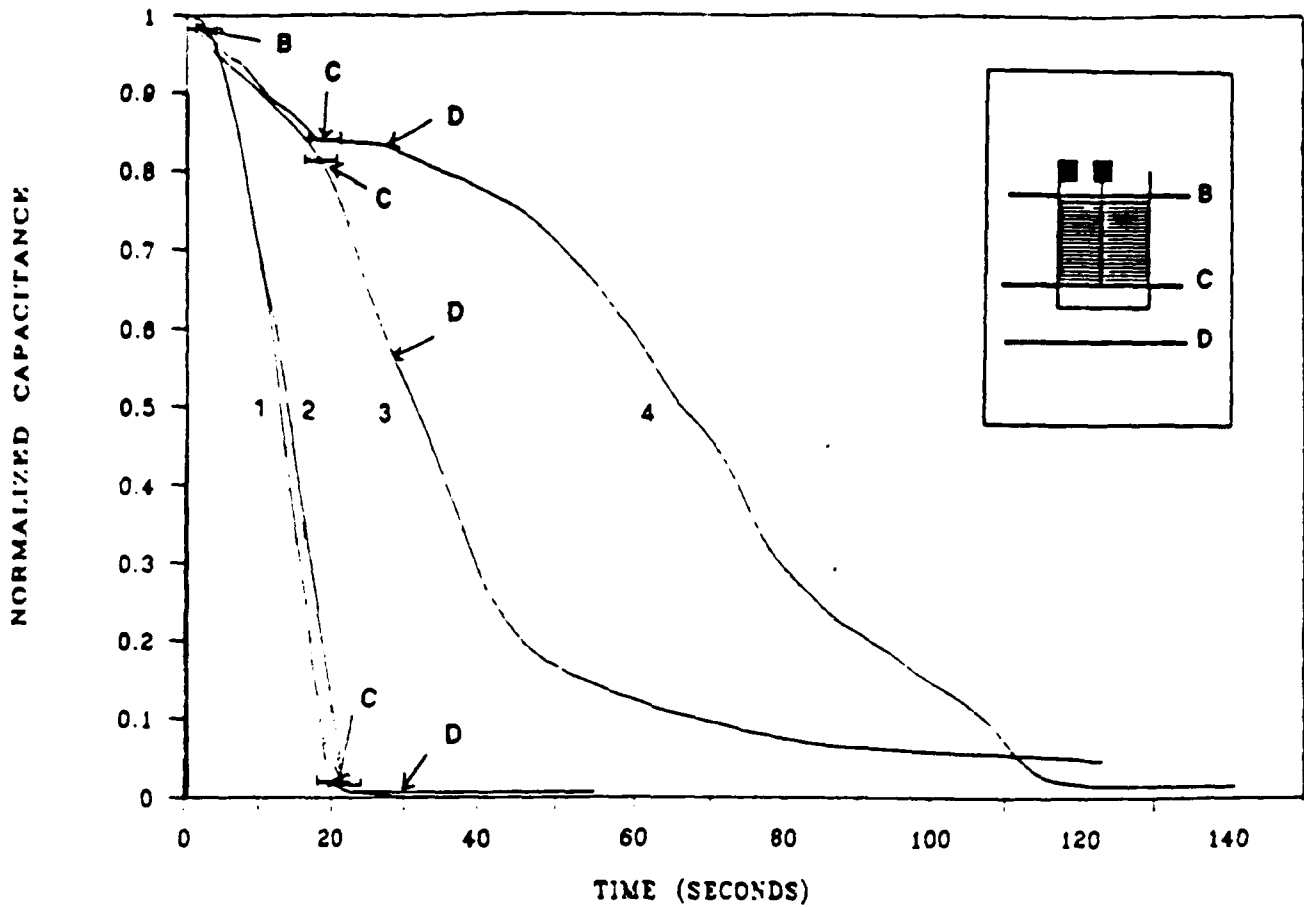


Figure 5. Measured capacitance of sensor versus time, for the upstrokes, at a speed of 0.27 mm/s. Curves 1, 2, 3 and 4 refer to no monolayer, arachidate, hemicyanine, and merocyanine, respectively. B, C and D in the inset show the positions of the sensor relative to the air-water interface at various stages of the stroke; the top finger of the sensor emerges at B, and the bottom finger at C; D denotes the end of the stroke. The error bars indicate the uncertainty in the determination of the points. The capacitance is normalized with the maximum value for the points. The deposition ratios for the strokes were 0.82, 0.95 and 0.98, for arachidate, merocyanine, and hemicyanine respectively.

Merocyanine dye was deposited over the same range of dipping speeds as the arachidate. Subphase entrainment occurred for all layers and increased with substrate dipping speed. As curve 4 in Fig. 5 shows, once the sensor was above the subphase, the capacitance decreased progressively toward the background value. No subphase was detected after the L/B film was allowed to equilibrate with dry air for a few minutes. When hemicyanine dye was deposited, subphase entrainment was also observed for all layers and the entrainment increased with dipping speed (curve 3, Fig. 5). Interestingly, the subphase was not removed from the film even after the sensor was equilibrated in air for 12 hrs. The entrained subphase could be removed by heating the sensor above 100° C for over 2 hrs.

The capacitance traces in Fig. 5 show that the deposition characteristics of the three monolayers at the same dipping speed are quite different, indicative of the influence of different factors.

CONCLUSION

Considerable progress was made in improving the quality of the films, yielding superlinear SHG with thickness. Degradation was studied and conclusively related to exposure to air. The capacitance sensor demonstrated its value by enabling the drying of the films to be detected, thus permitting us to determine the appropriate times for reinsertion of the substrate for subsequent deposition.

Since the completion of this contract, significant progress in these and other program activities has been achieved, demonstrating the value of pursuing organics and polymers for advanced applications in optics.

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